Generation and Synthetic Applications of Niobium-and Tantalum-Alkyne Complexes(Dissertation_全文)

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CHAPTER 1

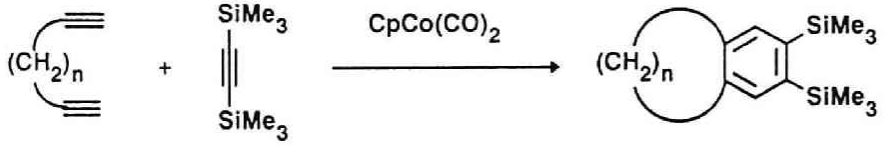
Introduction and General Summary

Organometallic compounds are finding increasing use in organic chemistry, both as reagents and as catalysts for carrying out a variety of synthesis. Of particular recent interest are organic reactions with high selectivities induced by low-valent early transition metals. The author has been interested in the use of metal-alkyne complexes of group 5 metals as a new reagent for selective construction of carbon skeletons. The present thesis describes the studies on synthetic reactions of alkynes mediated by low-valent niobium and tantalum; the studies are mainly focused on establishing the preparation of new reagents and applying them to carbon-carbon bond forming reactions.

In contrast to metal-alkene complexes, which were first isolated by Zeise in 1827, attempts to isolate the metal-alkyne complexes resulted in failure because of the rearrangement of the acetylenic proton.[1] In 1945, first isolation of the metal-alkyne complex $PtCl_2(HO(CH_3)_2CC{\equiv}CC(CH_3)_2OH)(py)$ was reported by Gel'man.[2] The structure of the complex was assumed by its elemental analysis and infrared spectrum. In the middle of 70s, the structure of the metal-alkyne complexes was determined by X-ray diffraction analysis and it made possible to ascertain the bindings between the central metal and ligands.[3] Nowadays, various metal-alkyne complexes of transition metals have been reported.[4]

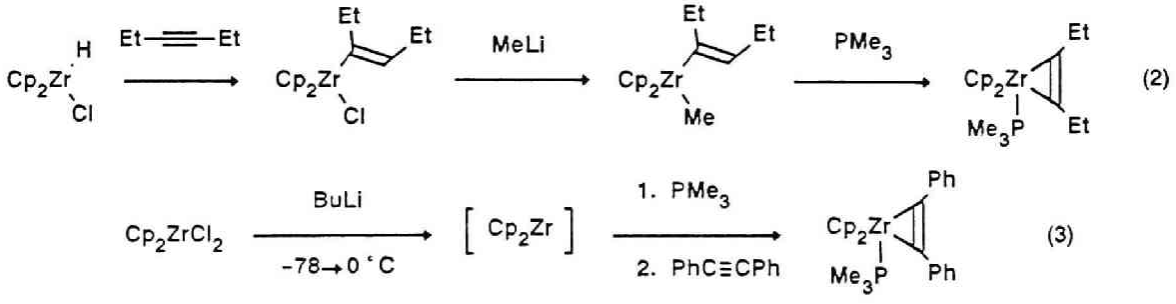
Reactivity of a carbon-carbon triple bond is either reduced or enhanced by coordination to a metal. Dicobalt hexacarbonyl is employed for the former purpose, which deactivate the triple bond by forming a metal-alkyne complex and hence to serve as a protecting group.[5] In contrast, insertion of an unsaturated molecule into a metal-carbon bond of a metal-alkyne complex takes place which

provides an important strategy for carbon–carbon bond formations. One of the typical examples is cyclotrimerization of alkynes to benzene derivatives. Yamazaki isolated the intermediate cobalt complexes and showed stepwise insertion of alkynes into a metal–carbon bond.[6] Because intermolecular version of cyclotrimerization of alkynes suffers from pair- and regioselectivity, Vollhardt developed intramolecular cyclotrimerization using $Me_3SiC{\equiv}CSiMe_3$ (eq 1).[7]

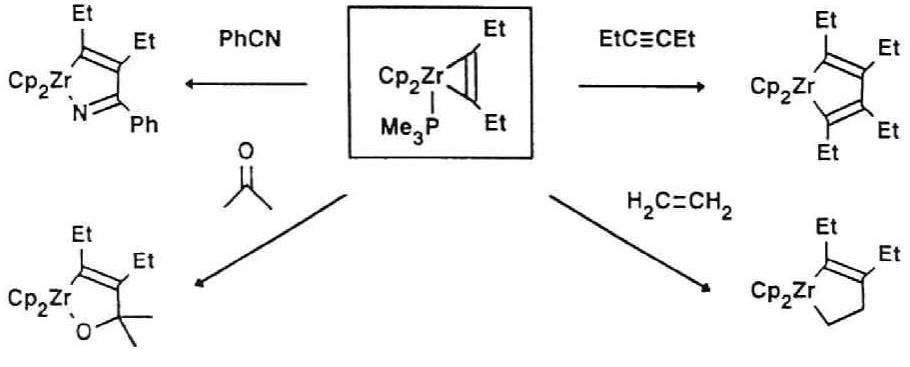


(1)

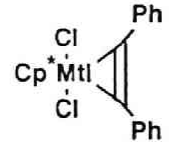
Recently, two groups, Buchwald[8] and Negishi,[9] discovered the convenient preparation of zirconocene–alkyne complexes (eq 2 and 3). They have provided novel coupling reactions between zirconocene–alkyne complexes and unsaturated compounds such as nitriles, alkynes, ketones, and aldehydes leading to the corresponding zirconacycles (Scheme 1).



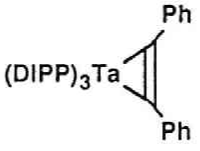
Scheme 1



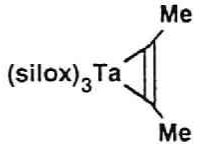
Group 5 metal–alkyne complexes are also isolated by several groups. The reactivity of complexes **1** and **2** toward unsaturated compounds was lower than that of zirconocene complexes.[10] Cyclotrimerization of alkynes leading to benzene derivatives with either catalytic or stoichiometric amount of low-valent group 5 metals has been reported.[11-13] Metal–alkyne complexes **3** and **4** were postulated as intermediates of cyclotrimerization of alkynes by Cotton[11] and Livinghouse,[13] respectively (eq 4 and 5). Tantalum–alkyne complex **5** having a DIPP ligand also promotes cyclotrimerization;[11] reactivity depends significantly on the number and nature of ligands. Related complex **6** having a bulky siloxy group was reported.[14]



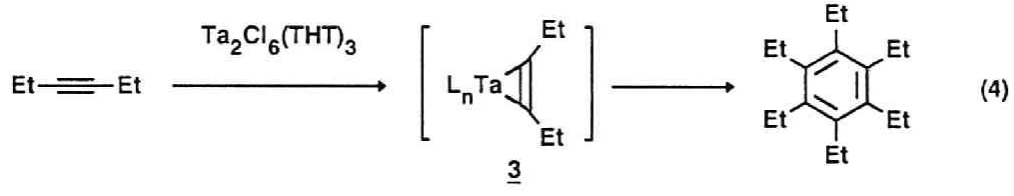
MtI = Nb (1)
Ta (2)
R. R. Schrock



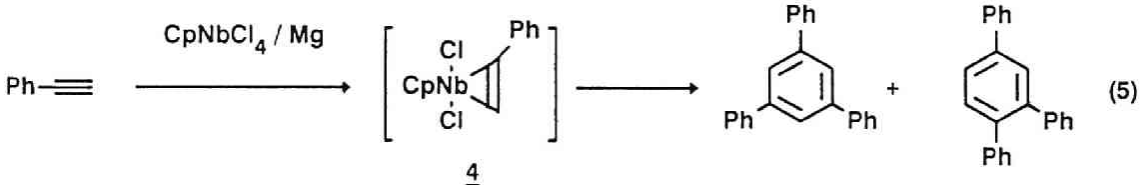
5
D. E. Wigley



6
P. T. Wolczanski

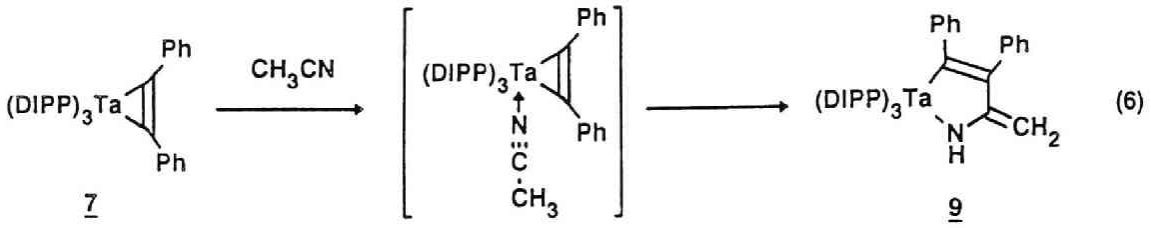


3

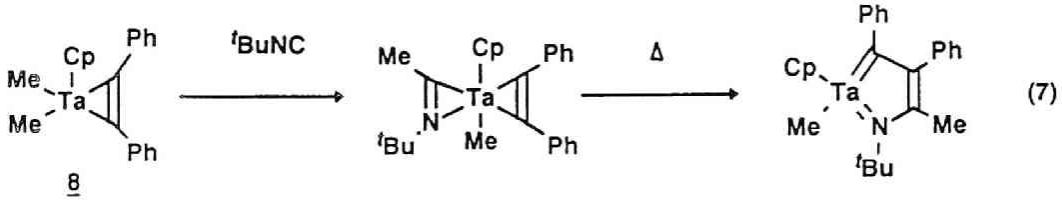


4

Insertion of nitriles[15] and isocyanide[16] into a tantalum–carbon bond of complexes **7** and **8** takes place to produce the corresponding tantalacycles **9** and **10**, respectively (eq 6 and 7). Although these insertion products possess potential utilities as synthetic intermediates, further studies directing to organic synthesis have not appeared.

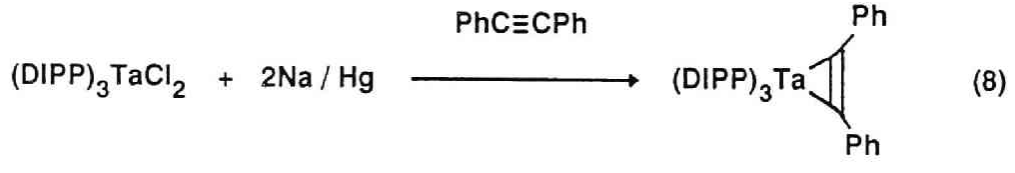


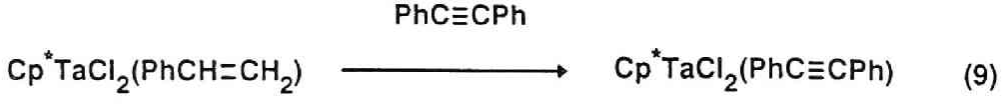
7 9



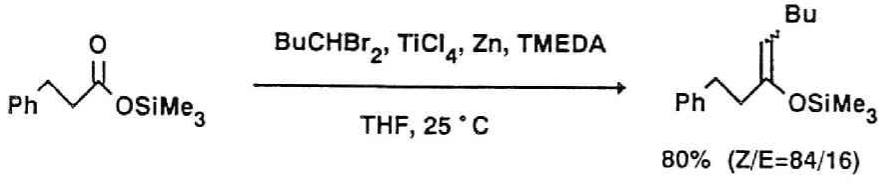
8 10

One of the major reasons why synthetic applications of the metal–alkyne complexes have not been extensively studied is that preparation of the reported group 5 metal–alkyne complexes requires to manipulate unstable reactive intermediates. Almost all metal–alkyne complexes have been prepared by one of two methods: reductive complexation of a low-valent metal with an acetylenic compound[11-16] or ligand substitution from a metal complex having an easily replaceable ligand.[10] In the case of niobium and tantalum, both methods were reported (eq 8 and 9).

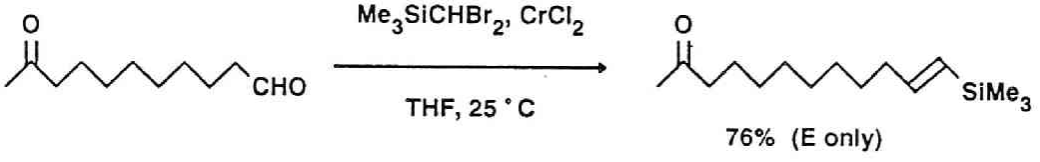




The author chose the former method by using commercially available $NbCl_5$ and $TaCl_5$, and tried to obtain low-valent niobium and tantalum by a simple reduction procedure. Although complexes having special ligands showed unique reactivity (*vide supra*), the author tried to use rather naked low-valent metals,[17] which were expected to produce more reactive complexes than the former reported ones. Third, and most of all, the author have learned how to produce low-valent metals such as titanium[18] and chromium[19] before starting this project (eq 10 and 11).



(10)

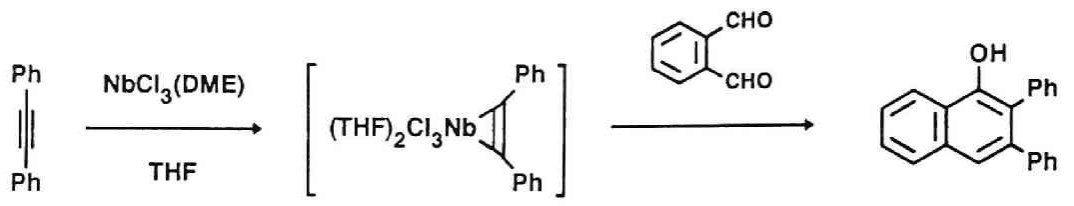


(11)

An interesting synthetic reaction using low-valent niobium appeared in 1982. Oshima reported the reduction of internal alkynes with low-valent niobium prepared by the reduction of $NbCl_5$ with $NaAlH_4$.[20] High *Z*-selectivity of the produced alkenes suggested the formation of niobium-alkyne complexes as an intermediate. However, quenching the mixture of the above reaction with D_2O did not give any deuterated olefin. This observation prompted us to reexamine the low-valent niobium chemistry under the conditions using a reducing agent having no hydride source.

After we have started the studies on niobium complexes, first synthetic application of niobium-alkyne complexes appeared in 1989.[21] Pedersen generated niobium-alkyne complexes by mixing the alkyne to $NbCl_3$(DME) and obtained

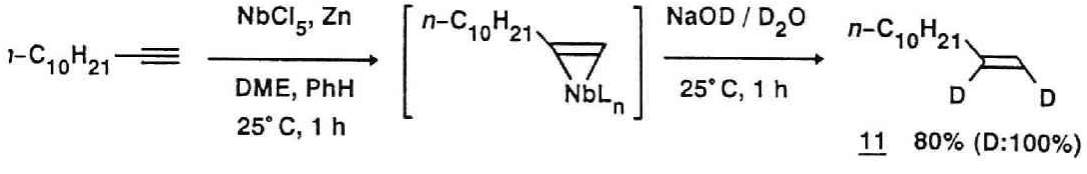
2,3-disubstituted 1-naphthols by reaction with phthalaldehyde (eq 12).



(12)

Independent to the reported results, the author performed his research to establish a widely applicable method for generation of group 5 metal-alkyne complexes and to develop novel and stereoselective carbon-carbon bond formations by using the complexes. In particular, much attention was paid to use the complex as a cis-fixed vicinal alkene dianion synthon. The general summary is following.

In Chapter 2, selective reduction of alkynes to (Z)-alkenes by means of low-valent niobium or tantalum is described. Low-valent niobium has rarely been used for organic synthesis until recently. The author discovered a convenient method for preparation of a low-valent niobium derived from $NbCl_5$ and zinc.[22] Partial reduction of alkynes can be achieved by using the low-valent niobium. Treatment of the reaction mixture with $NaOD-D_2O$ solution gives a vicinal dideuterated olefin. This observation suggests that a niobium-alkyne complex is formed as an intermediate (eq 13).



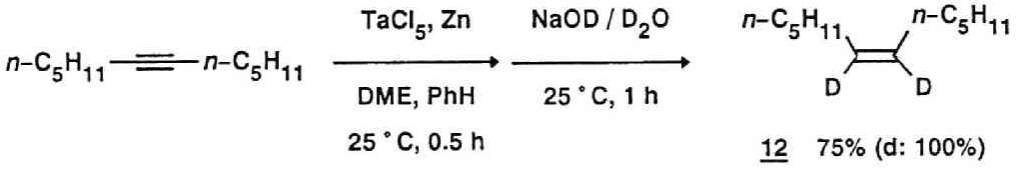
11 80% (D:100%)

(13)

Choice of the solvent is important for the formation of niobium-alkyne complexes. Reduction of $NbCl_5$ with zinc do not take place in a non-polar solvent

such as benzene and hexane, because the salt is insoluble to the solvent. Addition of polar solvent such as DME, THF, and HMPA to the non-polar one enhances the solubility of the salt. Among the combinations of polar- and non-polar solvents, a mixed solvent of DME and benzene (1:1) is the best solvent to generate niobium-alkyne complexes and to suppress cyclotrimerization of the alkynes. Complexation of a terminal alkyne with the low-valent niobium takes place in a mixture of DME and benzene (1:1). In the case of an internal alkyne, the reaction proceeds slowly due to the steric effect of substituent on alkyne. The reduction is accelerated by adding THF and HMPA instead of DME.

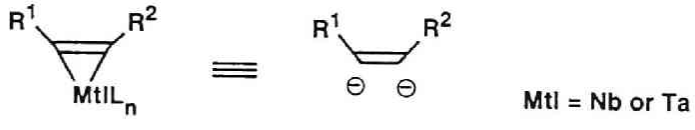
Low-valent tantalum can be produced from $TaCl_5$ and zinc by an analogous protocol to the niobium. Complexation of an internal alkyne with the low-valent tantalum proceeds faster compared to the case of low-valent niobium. Additionally, (*Z*)-selectivity of the produced alkene is higher than that with the niobium complex. A terminal alkyne is polymerized considerably with the low-valent tantalum. Quenching the reaction mixture of 6-dodecyne and a low-valent tantalum with alkaline D_2O solution gives a vicinal dideuterated olefin **12** (eq 14). Production of such dideuterated olefins **11** and **12** suggests potential use for the niobium- and tantalum-alkyne complex as a cis-fixed vicinal alkene dianion (Scheme 2).



(14)

12 75% (d: 100%)

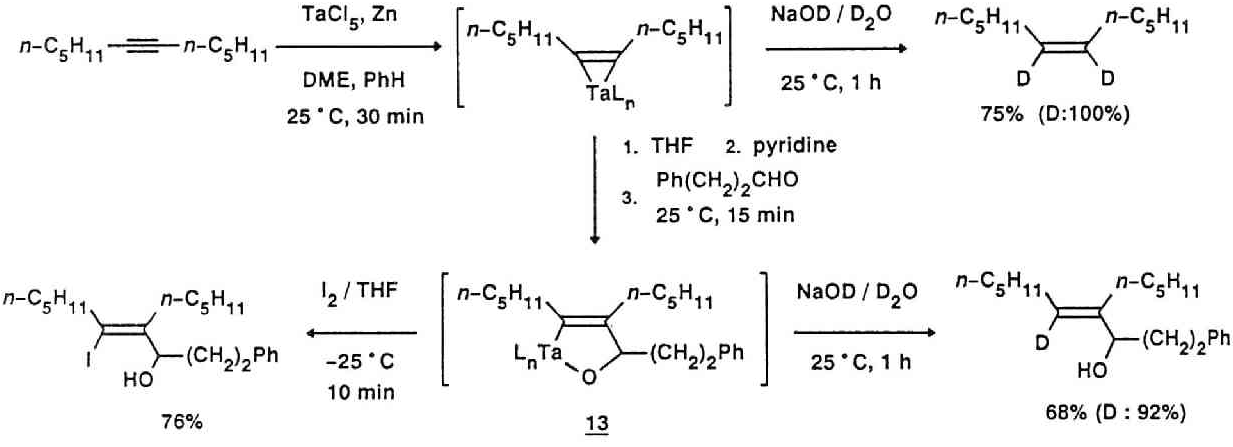
Scheme 2



Mtl = Nb or Ta

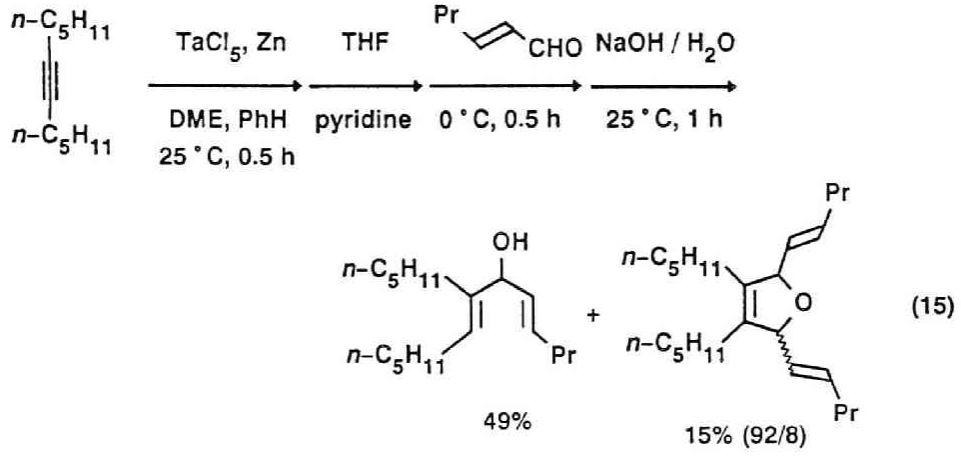
Chapter 3 discloses a novel carbon–carbon bond formation by the reaction of tantalum–alkyne complexes with carbonyl compounds. When tantalum–alkyne complexes, which are derived from alkynes and low-valent tantalum, are treated *in situ* with carbonyl compounds, (*E*)-allylic alcohols are produced stereoselectively after alkaline workup. Insertion of a carbonyl group into the tantalum–carbon bond gives an oxatantalacyclopentene complex **13** whose structure is suggested by the production of a deuterated allylic alcohol by alkaline workup with NaOD–D_2O. The complex **13** can be trapped with I_2 to give an iodo alcohol (Scheme 3).

Scheme 3



In the case of unsymmetrical alkynes, two regioisomeric allylic alcohols are produced. Regioselectivity of the reaction depends upon steric and electronic effects of the substituents on acetylenes. Insertion of a carbonyl group takes place at the less hindered site of the complex. When one of the substituent on acetylene becomes bulkier, higher regioselectivity is obtained. A reaction between an aromatic acetylene and carbonyl compounds takes place at the more hindered α-carbon of the phenyl group. High regioselectivity of the reaction with tantalum–alkyne complexes and aldehydes shows sharp contrast to the selectivities with zirconocene–alkyne complexes.

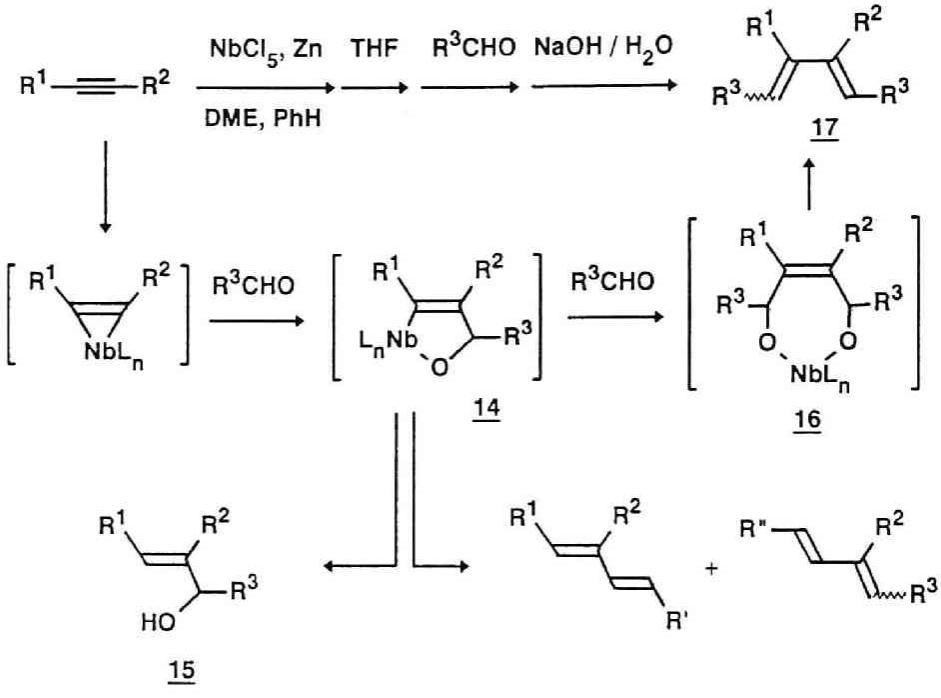
Treatment of a tantalum–alkyne complex with a β–substituted α,β–unsaturated aldehyde gives, however, a one–to–two addition product of the tantalum–alkyne complex and an aldehyde besides allylic alcohol (eq 15).



(15)

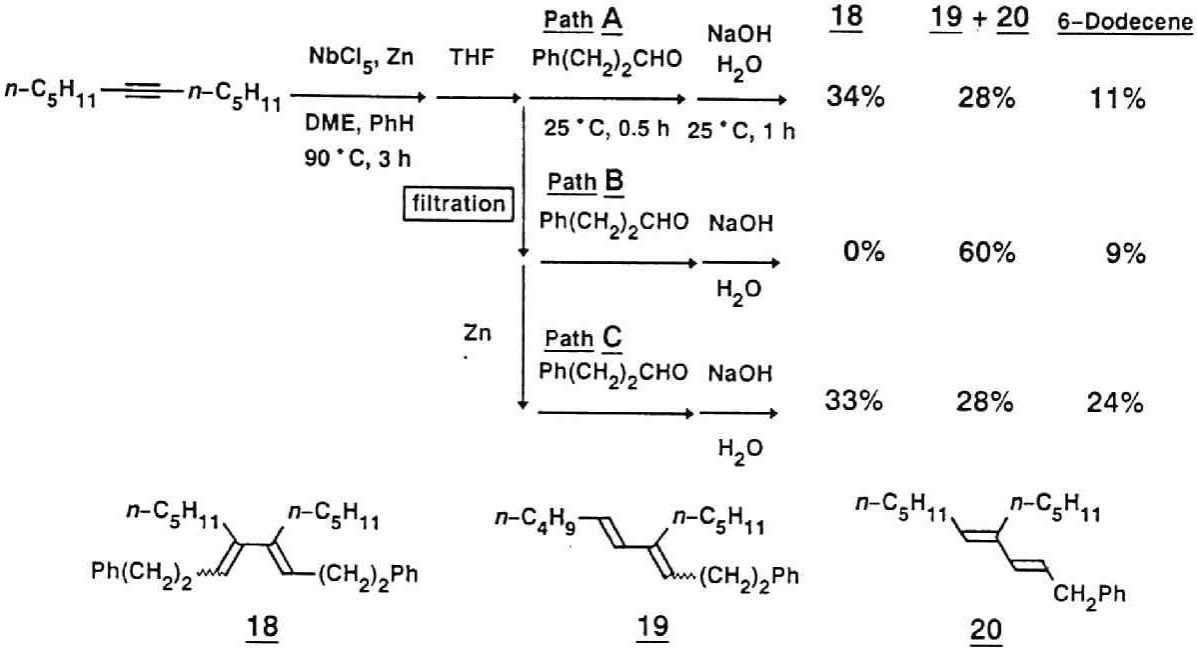
Unlike a tantalum–alkyne complex, a niobium–alkyne complex reacts with two equiv of aldehydes to give 1,3–diene derivatives, which is described in Chapter 4. The formation of 1,3–diene is explained by the following mechanism (Scheme 4). Insertion of an aldehyde into the niobium–carbon bond of the complex gives oxaniobacyclopentene complex **14**. Allylic alcohol **15** derived from hydrolysis of complex **14** can be observed at the early stage of the reaction. The second aldehyde subsequently inserts into the remained niobium–carbon (sp^2) bond to give the niobium salt of 2–butene–1,4–diol **16**. Deoxygenative elimination of two oxygens from the niobium salt **16** gives 1,3–diene **17**. Hydrolysis product of the niobium–diol complex **16** is not observed throughout the reaction. This observation suggests that deoxygenation proceeds very fast because of the strong oxophilicity of niobium. In contrast to the niobium case, reaction of a tantalum–alkyne complex with a β–substituted α,β–unsaturated aldehyde produces 2,5–dihydrofuran derivatives through uptake of one oxygen from dioxatantalacyclo–heptene (eq 15).

Scheme 4

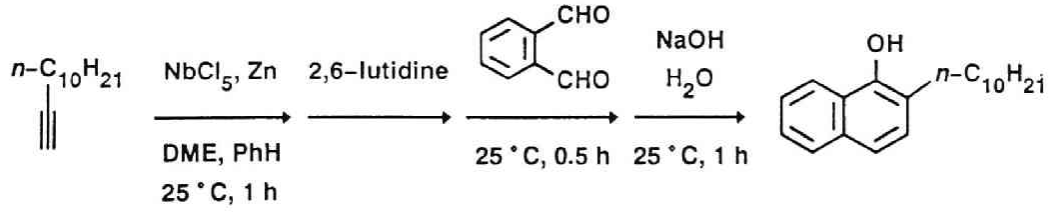


The presence of excess zinc is important to promote the 1,3-diene formation. Treatment of a niobium-6-dodecyne complex *in situ* with 3-phenylpropanal affords 1,3-diene **18** and a mixture of dehydration products **19** and **20** from a one-to-one adduct (Scheme 5). Use of filtered solution of the reaction mixture containing niobium-6-dodecyne complex before addition of the aldehyde gives only one-to-one adducts **19** and **20**; 1,3-diene **18** is not obtained. When zinc is added to the filtered solution of niobium-6-dodecyne complex, 1,3-diene **18** is produced by the reaction with the aldehyde. These results suggest that zinc is indispensable for the second insertion of an aldehyde into the niobacyclopentene complex **14** (Scheme 4). Reducing the niobium complex **16** with zinc is also needed for promoting the formation of **17** by deoxygenation from **16**.

Scheme 5



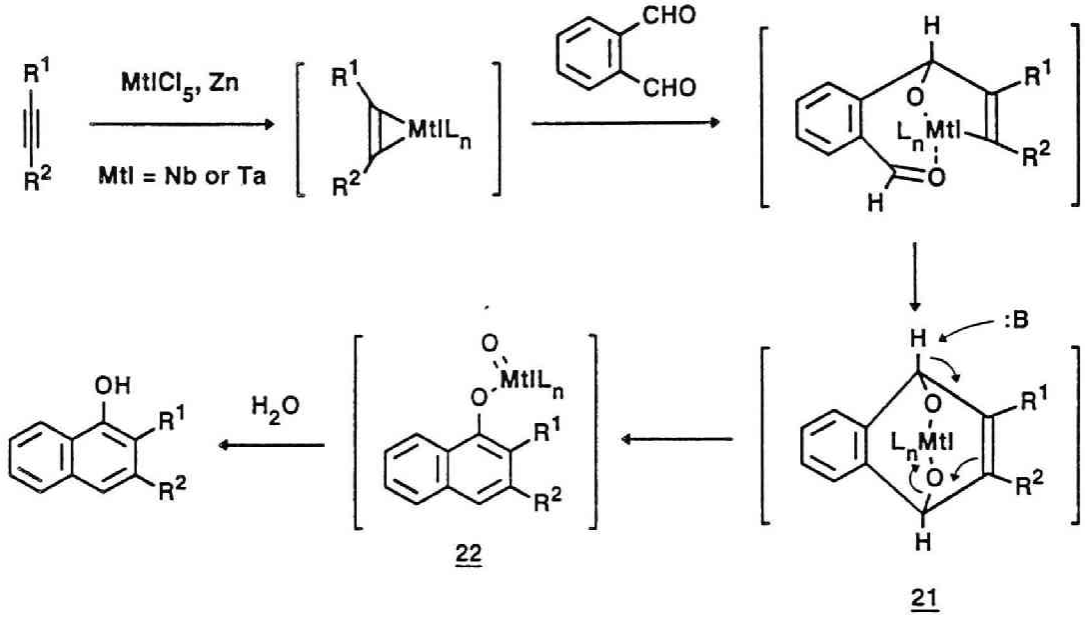
Chapter 5 discloses the synthesis of 1-naphthols by use of an alkyne complex. As niobium-alkyne complex reacts with 2 equiv of aldehyde, reaction between alkyne-complex and a dialdehyde which have two formyl groups at the appropriate position is examined. Treatment of niobium-1-dodecyne complex with phthalaldehyde gives 1-naphthol after alkaline workup. 2-Alkyl substituted 1-naphthols are produced regioselectively. Reaction of niobium-alkyne complexes derived from unsymmetrical alkynes with phthalaldehyde affords 1-naphthols having bulkier substituent at 3-position. The tantalum-alkyne complex reacts with two formyl groups of phthalaldehyde in contrast to selective formation of one-to-one adducts with mono aldehydes (eq 16). High regioselectivity is observed with the tantalum complexes.



(16)

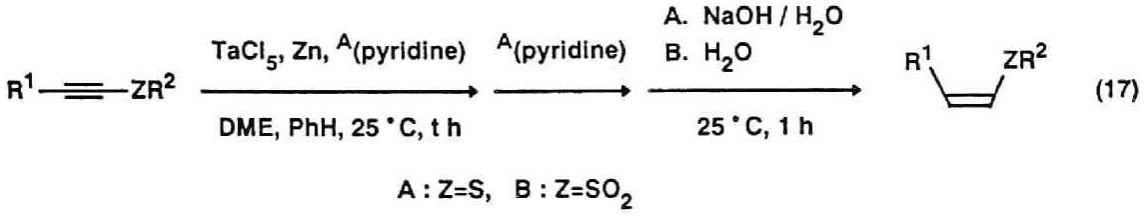
Plausible mechanism for the formation of 1-naphthol is shown in Scheme 6. Insertion of two formyl group into two carbon-metal bond of the alkyne complex gives **21**. Abstraction of a proton at the less hindered site promote aromatization; aqueous work-up of **22** produces 1-naphthol.

Scheme 6



To explore applicability of the formation of metal-alkyne complexes, several kinds of substituted acetylenes are examined. In Chapter 6, acetylenes having sulfenyl, sulfinyl, and sulfonyl groups are employed as starting materials. Treatment of an 1-alkynyl sulfide with a low-valent tantalum produces a tantalum-alkyne complex and 1-alkenyl sulfide is obtained after alkaline work up. Addition of pyridine to the low-valent tantalum before addition of alkynes prevents the formation of 1-chloro-1-alkenyl sulfide as a byproduct. Addition of another 20 equiv of pyridine before alkaline work up suppresses the isomerization. Although 3 equiv of the low-valent tantalum is required to complete the complexation of 1-alkynyl sulfone, (*Z*)-1-alkenyl sulfones are produced exclusively after work up with water (eq 17). On the contrary, a tantalum-1-

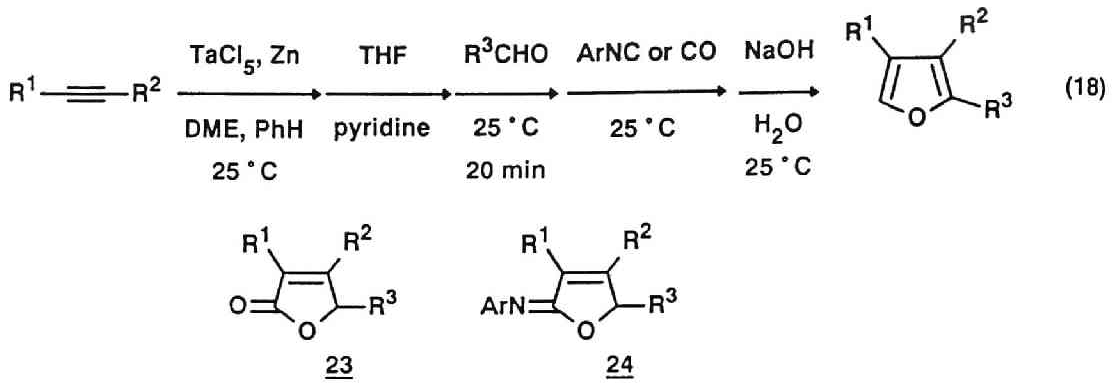
alkynyl sulfoxide complex can not be produced because sulfoxide is smoothly reduced into the corresponding sulfide under reaction conditions.



(17)

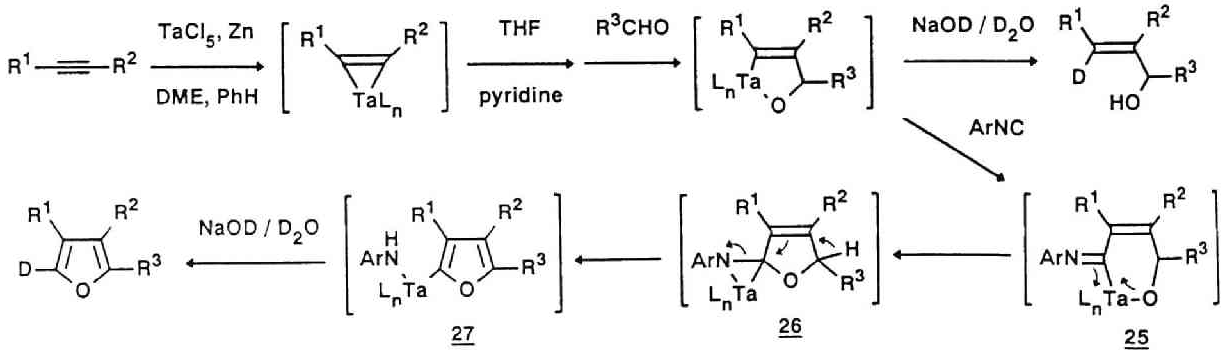
Tantalum–1–alkynyl sulfide and sulfone complexes react with an aldehyde to give two regioisomeric allylic alcohols. Regioselectivity of the reaction varies with the electronic nature of the substituents on acetylenes. Because of the electron–donating nature of the methylthio group, the alkyne complex from 1–dodecynyl methyl sulfide reacts with the carbonyl compound at only β–position of the sulfide group. Formation of α–adducts increases when an electron–withdrawing sulfonyl group is attached to an acetylene.

Chapter 7 discloses the preparation of highly substituted furans through insertion of an isocyanide into tantalum–carbon (sp^2) bonds of oxatantalacyclopentenes derived from tantalum–alkyne complexes and aldehydes. Insertion of carbon monoxide or isocyanides into metal–carbon bonds constitutes the important methods for introducing one carbon unit into organometallic compounds. Treatment of a mixture of an oxatantalacyclopentene with carbon monoxide or isocyanide gives a 2,3,4–trisubstituted furan (eq 18). Neither butenolide **23** nor imino lactone **24** is observed. Yields of furans are critically dependent on the amount of the isocyanide; excess isocyanide retards the formation of furans. Bulkier substituent of an acetylene possesses 4–position of the tri–substituted furan. This regioselectivity is determined at the formation of a oxatantalacyclopentene, which is described in Chapter 3.

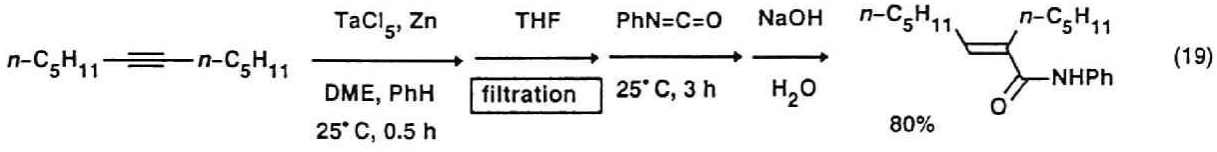


The following mechanism is assumed to form furan derivatives (Scheme 7). Insertion of an isocyanide into the carbon–tantalum bond of oxatantalacyclopentene produces a tantalacycle **25**. Migration of oxygen from tantalum to the imino carbon gives a η^2–acylimidoyl complex **26** *via* oxygen assisted rearrangement, which produces 2–furyltantalum **27**. The affinity of tantalum for heteroatoms and the high strain of azatantalacyclopropane in the η^2–acyl imidoyl complex **26** are the driving force for the migration process. Formation of 2–furyltantalum **27** is ascertained by the fact that quenching of the reaction mixture of **27** with alkaline D_2O afforded the 2–deuterated furan. Similar process, i.e. sequential insertion–deoxygenation, was observed by Buchwald in the reaction of azazirconacyclopentene with carbon monoxide (ca. 100 atm) which affords pyrroles.[23]

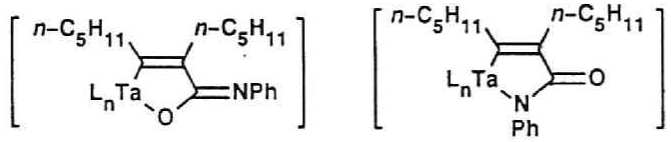
Scheme 7



Reactions of tantalum–alkyne complexes with several hetero–cumulenes are examined in Chapter 8. Treatment of a tantalum–alkyne complex with an isocyanate gives an α,β–unsaturated amide after alkaline work up (eq 19). Complex **28** or **29** is formed before workup.



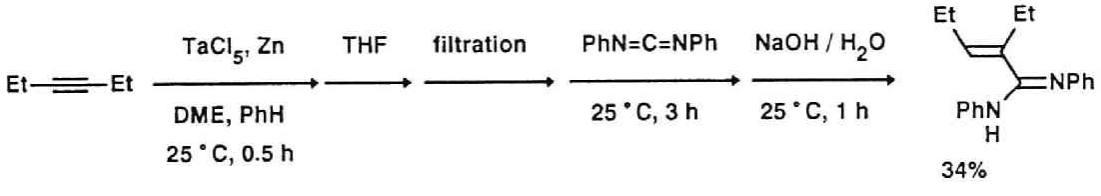
(19)



28 **29**

Filtration of the reaction mixture of tantalum–alkyne complexes under an argon atmosphere before addition of an isocyanate is indispensable to get high yields. Many byproducts appeared by avoiding the filtration, because zinc or low–valent tantalum in the reaction mixture promotes further reactions which consume the initial adduct **28** (or **29**).

Reaction of a tantalum–alkyne complex with phenyl thioisocyanate results in recovery of 6–dodecene. In contrast, tantalum–3–hexyne complex reacts with diphenyl carbodiimide to give (*E*)–α,β–unsaturated amidine (eq 20).



(20)

Instrumentation and Materials

Distillation of small amounts of products was performed with a Büchi Kugelrohr, and boiling points are indicated by an air bath temperature without correction. All melting points were determined by using a Yanaco MP-50929 melting points apparatus and are uncorrected. IR spectra were obtained with a JASCO IR-810 spectrometer. Mass spectra were obtained on a Hitachi M-80 mass spectrometer. ^{1}H and ^{13}C NMR were determined with a Varian XL-200 spectrometer. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane using the δ scale. Column chromatography was done with silica gel (Wakogel 200 mesh). GLPC was performed with a Hitachi 163 gas chromatograph using a Silicone OV-1 capillary column. Elemental analyses were performed by the staff at the Elemental Analyses Center of Kyoto University.

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Benzene, THF, and DME were distilled from sodium/benzophenone just before use. HMPA was distilled from calcium hydride and stored over 4A molecular sieves. TMEDA was distilled from potassium hydroxide. Zinc dust, purchased from Wako Pure Chemical Industries, Ltd. (GR grade), was activated by washing several times with 5% hydrochloric acid, washing in turn with water, methanol, and ether, and dried *in vacuo* according to the reported procedure.[22]

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Abbreviations

Ar	aryl
bp	boiling point
bs	broad singlet
Bu	butyl
ca.	*circa* (about)
Calcd	calculated
Cp	cyclopentadienyl
Cp^*	pentamethylcyclo–pentadienyl
d	doublet
DME	1,2–dimethoxyethane
DMF	*N,N*–dimethylformamide
Ed.	edition
eq	equation
equiv	equivalent
Et	ethyl
GLPC	gas liquid phase chromatography
h	hour(s)
HMPA	hexamethylphosphoric triamide
ibid.	*ibidem* (in the same space)
IR	Infrared (spectrum)
m	multiplet
M	molar (1M = 1 mol dm^{-1})
mCPBA	*m*–chloroperbenzoic acid
Me	methyl
min	minute(s)
mL	1 mL = 1 cm^{-3}
mmol	millimole
mp	melting point
MS	mass (spectum)
Mtl	metal
NMR	nuclear magnetic resonance
p. (pp.)	page(s)
Ph	phenyl
py	pyridine
q	quartet
R_f	relative mobility
ref.	reference
rt	room temperature
s	singlet
sec	second
t	triplet
temp	temperature
THF	tetrahydrofuran
TLC	thin layer chromato–graphy
TMEDA	*N,N,N′,N′*–tetra–methylethylenediamine
Torr	1 Torr = 133.322 Pa
T_r	retention time

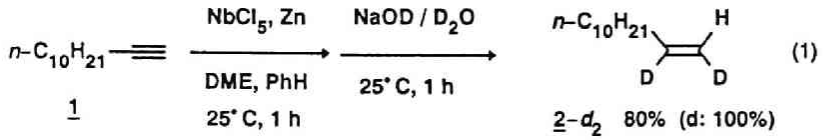
CHAPTER 2

Selective Reduction of Alkynes to (*Z*)-Alkenes *via* Niobium- or Tantalum-Alkyne Complexes.

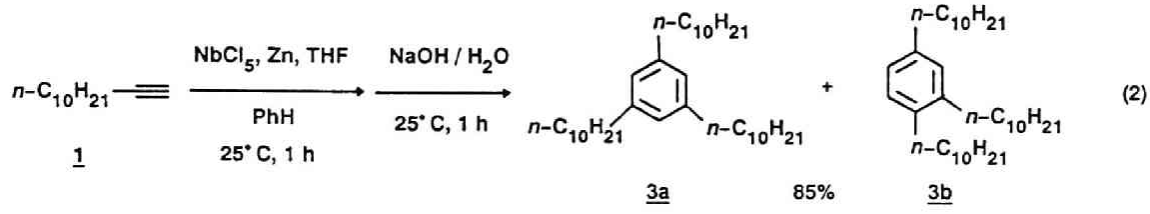
Niobium-alkyne complexes are prepared (not isolated) by treatment of alkynes with low-valent niobium derived from $NbCl_5$ and zinc in DME-benzene or THF-benzene-HMPA. Tantalum-alkyne complexes are produced by using $TaCl_5$ under the same conditions. Cyclotrimerization does not proceed in these solvent systems. Selective reduction of alkynes to (*Z*)-alkenes is achieved by hydrolysis of these metal-alkyne complexes with sodium hydroxide solution.

Because the rates of hydrogenation of double and triple bonds do not differ appreciably, several catalysts for partial hydrogenation of alkynes leading to (*Z*)-alkenes have been developed.[1] In contrast to hydrogenation, partial reduction of alkynes with sodium in liquid ammonia gives (*E*)-alkenes predominantly.[1] In 1982, we introduced low-valent niobium prepared by the reduction of $NbCl_5$ with $NaAlH_4$ and used it for some reductions, i.e. the pinacol-type reductive coupling of aldehydes or ketones and reduction of alkynes.[2] In the latter reaction with internal alkynes, high (*Z*)-alkene preference was recognized compared to $TiCl_4$-$LiAlH_4$ reagent.[3] This observation suggests the possibility of two reaction pathways. One possibility is the formation of a niobium-alkyne complex[4,5] as an intermediate. Pedersen isolated a one-to-one complex of niobium and an alkyne which is produced by treatment of the alkyne with $NbCl_3$(DME).[5] Another possibility is a hydrometalation pathway by Nb-H species.[6] However, quenching of the reaction mixture of an internal alkyne with D_2O did not give a deuterated olefin. Thus, we reexamined our previous niobium chemistry under the conditions using a reducing agent having no hydride source.[4,7]

In contrast to the previous $NbCl_5$-$NaAlH_4$ system,[2] a combination of $NbCl_5$ and zinc was found to give a vicinal dideuterated olefin after quenching the reaction mixture with NaOD-D_2O.[8,9] Treatment of 1-dodecyne with the combination of 4 equiv of $NbCl_5$ and 6 equiv of zinc in a solvent of DME-benzene (1:1) at 0 °C for 1 h followed by addition of alkaline D_2O afforded (*E*)-1,2-dideuterio-1-dodecene (**2-*d*$_2$**) in 81% yield (eq 1). The reaction course changed dramatically when a mixed solvent of benzene and THF (8 molar quantity of $NbCl_5$) was employed. Cyclotrimerization products of 1-dodecyne, a mixture of regioisomers **3a** and **3b**, was produced in 85% combined yields (eq 2).[4a,10]



(1)

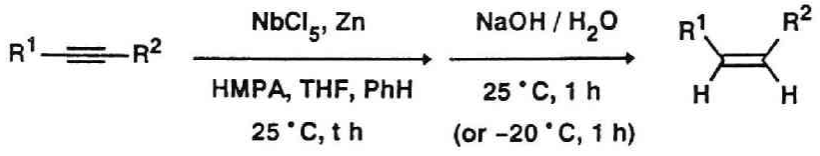


(2)

Aluminum powder was also effective for the reduction of $NbCl_5$. Ultrasonic irradiation to a mixture of $NbCl_5$ and aluminum in DME–benzene (1:1) before addition of alkyne was indispensable to get reproducible results.[11] Reduction of 1-dodecyne with the $NbCl_5$–Al system at 25 °C for 1.5 h afforded 1-dodecene in 89% yield, and quenching of the reaction mixture with NaOD–D_2O gave *cis*-dideuterated 1-dodecene (D: 100%). The reaction with a $NbCl_5$–magnesium system gave a complex mixture containing a small amount of the desired olefin.

Although heating was required to accomplish the complexation of alkynes with the low-valent niobium, the amount of $NbCl_5$ and zinc could be reduced to 1.0 and 1.5 equiv of the alkyne, respectively. For example, treatment of 6-dodecyne with 1.0 equiv of the $NbCl_5$ and 1.5 equiv of zinc at 25 °C for 24 h afforded (*Z*)-6-dodecene in 47% yield, along with unreacted 6-dodecyne in 27% yield.[12] Meanwhile, reaction of the same mixture at 90 °C for 6 h gave (*Z*)-6-dodecene in 81% yield. The latter 6-dodecene contains 87% of deuterium after workup with NaOD–D_2O. These observations suggest that a one-to-one complex[4b,13] of niobium and alkyne is produced as an intermediate.

Table 1. Reduction of Alkynes to (*Z*)-Alkenes by Means of a $NbCl_5$-Zn System[a]



Run	R^1	R^2	t / h	Yield / %[b]	Z / E[c]
1	n-$C_{10}H_{21}$	H	1	72[d]	--
2	Ph	H	2	81[d,e]	--
3	n-C_5H_{11}	n-C_5H_{11}	20	74	>99/<1
4	-$(CH_2)_{10}$-		7	82	>99/<1[f]
5	Ph	n-C_6H_{13}	20	86[g]	>99/<1[f]
6	c-C_6H_{11}	n-C_6H_{13}	40	81[g]	97/3
7	t-Bu	n-C_7H_{15} (**4**)	40	62[g]	97/3[h,i]
8	Me_3Si	n-$C_{10}H_{21}$ (**5**)	40	81[g]	96/4[f,h,j]

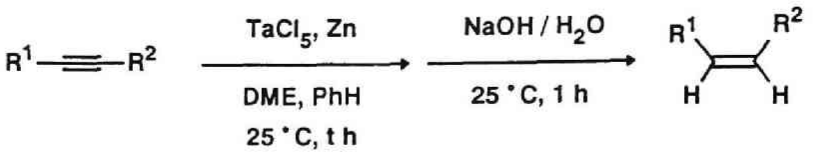
a) The alkyne (1.0 mmol) was treated at 25 °C with a reagent prepared from $NbCl_5$ (2.0 mmol), Zn (3.0 mmol), and HMPA (4.0 mmol) in THF-benzene (1:2). b) Isolated yields unless otherwise noted. c) The *Z*/*E* ratios were determined by capillary GLPC and/or ^1H NMR analysis of the corresponding epoxides unless otherwise noted. d) The reduction was conducted at 0 °C in DME-benzene (1:1); 4-fold excesses of low-valent niobium ($NbCl_5$ (4.0 mmol) and Zn (6.0 mmol)) were employed, as undesirable dimerization of the alkyne took place when unreacted alkyne remained. e) GLPC yield. f) The *Z*/*E* ratios were determined by capillary GLPC and/or ^1H NMR analysis of the product olefins. g) Mixed solvent of THF-benzene-HMPA (1:2:1) was employed to accelerate the reduction. h) The alkaline workup was conducted at −20 °C. i) The *Z*/*E* ratio of the product after workup at 25 °C was 89/11. j) The *Z*/*E* ratio of the product after workup at 25 °C was 93/7.

Reduction of internal alkynes with the low-valent niobium gave (*Z*)-alkenes predominantly. In the case of internal alkynes having bulky substituents, partial isomerization took place during the hydrolysis which was suppressed appreciably by doing the hydrolysis at low temperature (-20 °C, runs 7 and 8). The rate of the formation of niobium-alkyne complexes depends upon the solvent system, and the bulkiness of the substituents of alkynes. For example, in a mixed solvent of THF-benzene (1:2) and HMPA (double molar quantity of $NbCl_5$), 6-dodecene was produced in 74% yield by treatment with 2.0 equiv of $NbCl_5$ and 3.0 equiv of zinc for 20 h (run 3).[5,14] Alkynes **4** and **5** having bulky substituents such as *tert*-butyl and trialkylsilyl groups, decreased in reactivity. Thus, the amount of HMPA was increased to 25 vol % of the mixed solvent of THF-benzene-HMPA in the case of alkynes **4** and **5**.

Terminal alkynes porimerized with the low-valent niobium in the THF-benzene-HMPA system. Reduction of 1-dodecyne was conducted in DME-benzene (1:1), and the desired 1-dodecene was obtained in 72% yield (run 1). Styrene was also produced in 81% yield from phenylacetylene (run 2). These results show sharp contrast to the $NbCl_5$-$NaAlH_4$ system,[2] where reduction of terminal alkynes gave a complex mixture.

Low-valent tantalum[15] can be produced from $TaCl_5$ and zinc by an analogous protocol to the niobium system. Complexation of alkynes with the $TaCl_5$-Zn system proceeded faster than those with the $NbCl_5$-Zn system; (*Z*)-alkenes are produced after hydrolysis (Table 2). For example, the reduction of 6-dodecyne with $TaCl_5$-Zn system in DME and benzene (1:1) at 25 °C was finished within 0.5 h, while the same reduction with the $NbCl_5$-Zn system was not complete in 18 h.[12]

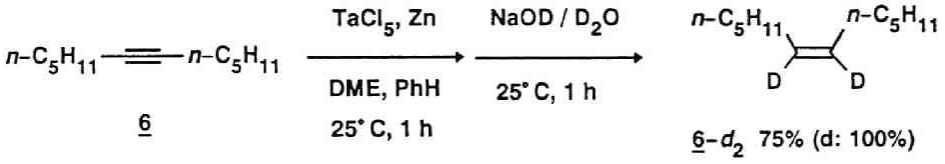
Table 2. Reduction of Alkynes to (Z)-Alkenes by Means of a $TaCl_5$-Zn System[a]



Run	R^1	R^2	t / h	Yield / %[b]	Z / E[c]
1	n-$C_{10}H_{21}$	H	0.3	39	--
2	n-$C_{10}H_{21}$	H	1	52[d]	--
3	Ph	H	1	68[e]	--
4	n-C_5H_{11}	n-C_5H_{11}	0.5	85	>99/<1
5	$-(CH_2)_{10}-$		0.3	69	>99/<1[f]
6	Ph	n-C_6H_{13}	0.5	85	>99/<1[f]
7	c-C_6H_{11}	n-C_6H_{13}	4	80	>99/<1
8	t-Bu	n-C_7H_{15}	4.5	82[g]	>99/<1
9	Me_3Si	n-$C_{10}H_{21}$	2	79	89/11[f]
10	Bu	CH_2=$CH(CH_2)_3$	0.6	81[h]	>99/<1
11	n-$C_{10}H_{21}$	CH_2=$CH(CH_2)_4$	0.6	82[h]	>99/<1
12	n-$C_{10}H_{21}$	$HO(CH_2)_4$	0.5	80	>99/<1

a) The alkyne (1.0 mmol) was treated at 25 °C with a reagent prepared from $TaCl_5$ (2.0 mmol) and Zn (3.0 mmol) in DME-benzene (1:1). b) Isolated yields unless otherwise noted. c) The *Z/E* ratios were determined by capillary GLPC and/or ^1H NMR analysis of the corresponding epoxides unless otherwise noted. d) One equiv of $TaCl_5$ and 1.5 equiv of zinc were employed. Two equiv of TMEDA was added before addition of 1-dodecyne. Dodecane was produced in 2% yield. e) GLPC yield. f) The *Z/E* ratios were determined by capillary GLPC and/or ^1H NMR analysis of the product olefins. g) Four equiv of $TaCl_5$ and 6 equiv of zinc were used, as the alkyne remained with the standard amounts of the reagent. h) Internal alkene was produced in about 5% through overreduction of a terminal double bond.

Isomerization to (*E*)-alkenes was suppressed except in the case of a silylalkyne (runs 7-9), when low-valent tantalum was employed. Quenching the reaction mixture of the reduction of 6-dodecyne with the low-valent tantalum by the addition of NaOD-D_2O gave also a vicinal dideuterated olefin **6-d_2** in 75% yield (eq 3). Terminal alkynes are too reactive with the $TaCl_5$-Zn reagent, and the yield with the tantalum reagent was lower than that with the niobium reagent (run 1). Best yield was obtained when 2.0 equiv of TMEDA was added before addition of 1-dodecyne (run 2).



(3)

Olefinic double bonds which were capable of participating in a cyclization remained intact (runs 10 and 11). This observation shows a sharp contrast to the reaction with low-valent zirconium.[16] Reduction of an alkyne having a hydroxyl group was performed in excellent yield (run 12).

Low-valent group 5 metals react with alkynes to form metal-alkyne complexes.[4,5,7,10,18] Since low-valent group 5 metal complexes are reported to catalyze cyclotrimerization of acetylenes,[4a,10] it is of considerable interest that no benzene derivative was observed throughout the reaction in DME-benzene (1:1). Introduction of deuterium at a *cis*-vicinal position of alkenes suggests that the niobium- and tantalum-alkyne complexes reported here are capable to use as a *cis* vicinal dianion reagent.[18]

Experimental Section

Preparation of Internal Alkynes. Internal alkynes were prepared according to the standard procedure described in ref. 19.

1-Phenyl-1-octyne.[20] To a stirred solution of phenylacetylene (1.6 g, 16 mmol) and HMPA (2.8 mL, 16 mmol) in THF (16 mL) at 0 °C under an argon atmosphere was added butyllithium (10 mL of 1.6 M hexane solution, 16 mmol) dropwise over a period of 10 min. After the reaction mixture was stirred at 0 °C for 15 min, 1-bromohexane (2.6 g, 16 mmol) was added to the mixture; the resulting mixture was stirred at 0 °C for an additional 1 h. The mixture was poured into ice-cold water and extracted with hexane. The organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Distillation of the crude product gave 2.6 g (88%) of 1-phenyl-1-octyne. ^1H NMR ($CDCl_3$): δ 0.88 (t, J=7.0 Hz, 3H), 1.2-1.5 (m, 4H), 1.3-1.6 (m, 2H), 1.5-1.7 (m, 2H), 2.40 (t, J=6.9 Hz, 2H), 7.2-7.5 (m, 5H).

1-Cyclohexyl-1-octyne. Triphenylphosphine (13 g, 50 mmol) was added to a stirred solution of tetrabromomethane (17 g, 50 mmol) in dichloromethane (100 mL) at 0 °C under an argon atmosphere. The mixture was stirred at 0 °C for 2 h. Zinc (3.3 g, 50 mmol) was added to the reaction mixture at 25 °C, and the resulting mixture was stirred at 25 °C for 20 h. Cyclohexanecarbaldehyde (2.8 g, 25 mmol) was added at 25 °C to the mixture, and the whole mixture was stirred at 25 °C for an additional 30 min. Hexane was added to the reaction mixture, and the insoluble material was removed by filtration. The filtrates were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Distillation of the crude product gave 6.4 g (95%) of 1,1-dibromo-2-cyclohexylethene. To the solution of 1,1-dibromo-2-cyclohexylethene (6.4 g, 24 mmol) in THF (120 mL) under an argon atmosphere at -78 °C was added butyllithium (30 mL of 1.6 M hexane solution, 48 mmol).

After stirred at −78 °C for 1 h, the reaction mixture was warmed to 25 °C, and stirred at 25 °C for 1 h. HMPA (4.2 mL, 24 mmol) and 1−iodohexane (5.1 g, 24 mmol) were added to the reaction mixture at 0 °C. The mixture was stirred at 0 °C for 1 h and at 25 °C for 1 h. The mixture was poured into ice−cold water, extracted with hexane, and washed with brine. The organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Distillation of the crude product gave 2.2 g (47%) of 1−cyclohexyl−1−octyne as a colorless liquid.[21] Bp 85−86 °C (0.60 Torr); IR (neat): 2926, 2852, 2340, 1378, 1298, 888 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.89 (t, *J*=6.6 Hz, 3H), 1.2−1.5 (m, 8H), 1.3−1.7 (m, 6H), 1.6−1.9 (m, 4H), 2.15 (t, *J*=6.4 Hz, 2H), 2.2−2.4 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 18.8, 22.6, 25.0, 26.0, 28.5, 29.2, 31.4, 33.2, 80.1, 84.6; MS *m/z* (rel intensity): 192 (M^+; 6), 93 (62), 81 (87), 67 (100), 41 (46). Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.40; H, 12.39.

2,2−Dimethyl−3−undecyne (4). The title compound was prepared in 80% yield from 3,3−dimethyl−1−butyne and 1−bromoheptane in the similar manner described above. Bp 86−87 °C (bath temp, 14 Torr); IR (neat): 2926, 2856, 2340, 1734, 1458, 1362, 1266 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.89 (t, *J*=7.0 Hz, 3H), 1.19 (s, 9H), 1.2−1.6 (m, 10H), 2.12 (t, *J*=6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 14.1, 18.6, 22.6, 27.3, 28.7, 28.8, 29.2, 31.5, 31.8, 78.5, 88.9; MS *m/z* (rel intensity): 180 (M^+, 1), 123 (30), 109 (69), 95 (100), 81 (82), 67 (51), 55 (42). Anal. Calcd for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 86.53; H, 13.66.

1−Trimetylsilyl−1−dodecyne (5). The title compound was prepared in 89% yield from 1−dodecyne and chlorotrimethylsilane in the similar manner without HMPA. Bp 75 °C (0.15 Torr); IR (neat): 2924, 2852, 2172, 1466, 1249, 841, 758 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.14 (s, 9H), 0.87 (t, *J*=6.4 Hz, 3H), 1.2−1.5 (m, 14H), 1.4−1.6 (m, 2H), 2.20 (t, *J*=7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 0.2, 14.1, 19.9, 22.7, 28.7, 28.8, 29.1, 29.4, 29.5, 29.6, 32.0, 84.2, 107.7; MS *m/z* (rel intensity) 238 (M^+,

0.4), 223 (69), 154 (11), 73 (100), 59 (42). Anal. Calcd for $C_{15}H_{30}Si$: C, 75.54; H, 12.68. Found: C, 75.28; H, 12.63.

1-Undecen-6-yne. *p*-Toluenesulfonyl chloride (14 g, 75 mmol) was added at -30 °C to a stirred solution of 4-penten-1-ol (4.3 g, 50 mmol) in pyridine (100 mL). After being stirred at -30 °C for 30 min, the reaction mixture was poured into ice-cold water and extracted with ethyl acetate. The organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Sodium iodide (23 g, 150 mmol) was added at 25 °C to a solution of the crude mixture in acetone (100 mL). The mixture was heated at reflux (70 °C) for 3 h. The resulting mixture was poured into ice-cold water and extracted with hexane. The organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by column chromatography on silica gel using hexane as eluent gave 5.1 g (52%) of 5-iodo-1-pentene as a liquid. The title compound was prepared in 64% yield from 5-iodo-1-pentene and 1-hexyne. Bp 87-88 °C (bath temp, 15 Torr); IR (neat): 2928, 2858, 2370, 1730, 1655, 1459, 1437, 1331, 911 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.90 (t, *J*=7.3 Hz, 3H), 1.3-1.6 (m, 4H), 1.51 (tt, *J*=11.6, 11.6 Hz, 2H), 2.0-2.4 (m, 6H), 4.97 (d, *J*=10.3 Hz, 1H), 5.03 (d, *J*=17.1 Hz, 1H), 5.80 (ddt, *J*=10.3, 17.1, 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 13.6, 18.1, 18.4, 21.9, 28.3, 31.2, 32.8, 79.6, 80.4, 114.9, 138.0; MS *m/z* (rel intensity): 150 (M^+, 0.3), 135 (11), 108 (46), 93 (100), 79 (70), 67 (41), 41 (40). Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.99; H, 12.09.

1-Octadecen-7-yne. The title compound was prepared in 53% yield from 1-dodecyne and 6-iodo-1-hexene. Bp 106-109 °C (0.20 Torr); IR (neat): 2924, 2852, 2355, 1641, 1458, 991, 909 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0,88 (t, *J*=6,8 Hz, 3H), 1.1-1.4 (m, 14H), 1.3-1.7 (m, 6H), 2.0-2.2 (m, 6H), 4.94 (d, *J*=10.2 Hz, 1H), 5.01 (d, *J*=17.1 Hz, 1H), 5.81 (ddt, *J*=10.2, 17.1, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 18.6, 18.8, 22.7, 28.1, 28.6, 28.9, 29.2, 29.4, 29.6, 31.9, 33.3, 79.9, 80.4,

114.5, 138.7; MS *m/z* (rel intensity): 248 (M^+, 0.5), 149 (37), 122 (72), 107 (86), 79 (100), 41 (91). Anal. Calcd for $C_{18}H_{32}$: C, 87.02; H, 12.98. Found: C, 87.22; H, 12.97.

5-Octadecyn-1-ol.[22] To a stirred solution of 5-hexyn-1-ol (2.0 g, 20 mmol) in DMF (8 mL) were added at 0 °C imidazole (3.4 g, 50 mmol) and *tert*-butylchlorodimethylsilane (3.6 g, 24 mmol). After being stirred at 25 °C for 2.5 h, the reaction mixture was poured into water and extracted with hexane. The organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel using hexane as eluent gave 4.1 g (96%) of *tert*-butyldimethylsilyl 5-hexynyl ether. To a stirred solution of the *tert*-butyldimethylsilyl 5-hexynyl ether(4.1 g, 19 mmol) in THF (19 mL) and HMPA (3.3 mL, 19 mmol) at 0 °C under an argon atmosphere was added butyllithium (12 mL of 1.6 M hexane solution, 19 mmol) dropwise over a period of 10 min. After the reaction mixture was stirred at 0 °C for 15 min, a solution of 1-iodododecane (5.9 g, 20 mmol) in THF (20 mL) was added to the reaction mixture, and the resulting mixture was stirred for an additional 1 h. The mixture was poured into ice-cold water and extracted with hexane. The organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Distillation of the crude product gave 3.8 g (52%) of *tert*-butyldimethylsilyl 5-octadecynyl ether. To a stirred solution of *tert*-butyldimethylsilyl 5-octadecynyl ether (3.8 g, 10 mmol) in THF (50 mL) was added at 25 °C a THF solution of tetrabutylammonium fluoride (1.0 M, 30 mL, 30 mmol). After being stirred at 25 °C for 20 min, the reaction mixture was poured into water and extracted with ether. The organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel using ethyl acetate-hexane (1:3) as eluent gave 2.4 g (91%) of 5-octadecyn-1-ol as a colorless liquid: ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.8 Hz, 3H), 1.1-1.4 (m, 19H), 1.3-1.8 (m, 6H), 2.1-2.3 (m, 4H), 3.67 (t,

J=6.3Hz, 2H).

Reduction of 1-Dodecyne with a $NbCl_5$-Zn System. In a 50-mL reaction flask was placed $NbCl_5$ (1.1 g, 4.0 mmol) under an argon atmosphere. To the salt were added at 25 °C benzene (5 mL) and DME (5 mL) successively. Zinc dust (0.39 g, 6.0 mmol) was added to the stirring pale orange solution of $NbCl_5$, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned to dark brown with slightly exothermic process. To the mixture was added at 0 °C a solution of 1-dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 0 °C for 1 h. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The precipitated white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The combined filtrate and washings were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel with hexane as eluent gave 0.12 g (72%) of 1-dodecene.

Reduction of 1-Dodecyne with a $TaCl_5$-Zn System. In a 50-mL reaction flask was placed $TaCl_5$ (0.36 g, 1.0 mmol) under an argon atmosphere. To the salt were added at 25 °C benzene (2.5 mL) and DME (2.5 mL) successively. Zinc dust (0.10 g, 1.5 mmol) was added to the stirring pale yellow solution of $TaCl_5$ and the mixture was stirred at 25 °C for 20 min, TMEDA (0.23g, 2.0 mmol) was added to the mixture, and the resulting mixture was stirred at 25 °C for 20 min. To the mixture was added at 25 °C a solution of 1-dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C for 1 h. Aqueous NaOH solution (15%, 2mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The crude product was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column

chromatography on silica gel with hexane as eluent gave 87 mg (52%) of 1-dodecene as a colorless liquid.

Reduction of Phenylacetylene with Low-Valent Niobium. The reduction of phenylacetylene was carried out similarly. The yield of styrene was determined by capillary GLPC (column temp 60 °C, t_r=4.32 min) using nonane as an internal standard.

Reduction of Phenylacetylene with Low-Valent Tantalum. To a stirred solution of $TaCl_5$ (0.36 g, 1.0 mmol) in DME and benzene (1:1, 5 mL) was added zinc dust (0.10 g, 1.5 mmol) at 25 °C under an argon atmosphere, and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of phenylacetylene (0.10 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C for 30 min. Aqueous NaOH solution (15%, 2mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The yield of styrene was determined by capillary GLPC.

Typical procedure for Partial Reduction of an Internal Alkyne with a $NbCl_5$-Zn System. Procedure A: To a stirred solution of $NbCl_5$ (1.1 g, 4.0 mmol) in DME and benzene (1:1, 10 mL) was added zinc dust (0.39 g, 6.0 mmol) under an argon atmosphere, and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C for 5.5 h. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The precipitated white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The filtrate and washings were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel with hexane as eluent gave 0.13 g (80%) of

6-dodecene. **(b) Procedure B:** To a stirred pale orange solution of $NbCl_5$ (0.54 g, 2.0 mmol) in THF and benzene (1:2, 15 mL) were added HMPA (0.70 mL, 4.0 mmol) and zinc dust (0.20 g, 3.0 mmol) successively under an argon atmosphere, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned from purple to dark blue with slightly exothermic process. To the mixture was added at 25 °C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in THF and benzene (1:2, 1.5 mL), and the resulting mixture was stirred at 25 °C for 20 h. Aqueous NaOH solution (15%, 2 mL) was added at 25 °C, and the whole mixture was stirred at 25 °C for an additional 1 h. The precipitated white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The filtrate and washings were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel with hexane as eluent gave 0.12 g (74%) of 6-dodecene. **(c) Procedure C:** To a stirred pale orange solution of $NbCl_5$ (0.54 g, 2.0 mmol) in a mixed solvent of THF, benzene, and HMPA (1:2:1, 20 mL) was added zinc dust (0.20 g, 3.0 mmol) under an argon atmosphere, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned from wine red to dark purple. To the mixture was added at 25 °C a solution of 1-phenyl-1-octyne (0.19 g, 1.0 mmol) in THF and benzene (1:2, 1.5 mL), and the resulting mixture was stirred at 25 °C for 20 h. Aqueous NaOH solution (15%, 2 mL) was added at 25 °C, and the whole mixture was stirred at 25 °C for an additional 1 h. The precipitated white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The filtrate and washings were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel with hexane as eluent gave 0.16 g (86%) of 1-phenyl-1-octyne.

Typical Procedure for Partial Reduction of an Internal Alkyne with a $TaCl_5$-Zn System. To a stirred solution of $TaCl_5$ (0.72 g, 2.0 mmol) in DME and

benzene (1:1, 10 mL) was added zinc dust (0.20 g, 3.0 mmol) at 25 °C under an argon atmosphere, and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the resulting mixture was stirred at 25 °C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added, and the whole mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The crude product was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel with hexane as eluent gave 0.14 g (85%) of 6-dodecene.

(*Z*)-6-Dodecene. The title compound was produced by the reduction with either a $NbCl_5$-Zn system (procedure A or B) or a $TaCl_5$-Zn system. The *E*/*Z* ratio was determined by ^{1}H NMR analysis of the corresponding epoxide.[23]

(*Z*)-Cyclododecene. The title compound was prepared by the reduction with either a $NbCl_5$-Zn system (procedure B) or a $TaCl_5$-Zn system. The *E*/*Z* ratio was determined by capillary GLPC (90 °C, t_r=9.8 min (*E*) and 10.5 min (*Z*)).

(*Z*)-1-Phenyl-1-octene.[20] The title compound was produced by the reduction with either a $NbCl_5$-Zn system (procedure B) or a $TaCl_5$-Zn system. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, *J*=6.8 Hz, 3H), 1.1-1.6 (m, 8H), 2.2-2.4 (m, 2H), 5.67 (dt, *J*=11.6, 7.3 Hz, 1H), 6.41 (d, *J*=11.6 Hz, 1H), 7.1-7.4 (m, 5H). The *E*/*Z* ratio was determined by ^{1}H NMR analysis. **(*E*)-1-Phenyl-1-octene.** ^{1}H NMR ($CDCl_3$): δ 0.90 (t, *J*=6.8 Hz, 3H), 1.2-1.8 (m, 8H), 2.25 (dt, *J*=6.5, 6.8 Hz, 2H), 6.23 (dt, *J*=15.9, 6.5 Hz, 1H), 6.39 (d, *J*=15.9 Hz, 1H), 7.1-7.5 (m, 5H).

(*Z*)-1-Cyclohexyl-1-octene. The title compound was produced by the reduction with either a $NbCl_5$-Zn system (procedure C) or a $TaCl_5$-Zn system. Bp 62-63 °C (bath temp, 1 Torr); IR (neat): 2922, 2848, 1730, 1449, 1379, 1269, 889 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.89 (t, *J*=6.5 Hz, 3H), 1.0-1.2 (m, 2H), 1.1-1.5 (m,

12H), 1.5–1.9 (m, 4H), 1.9–2.2 (m, 2H), 2.2–2.4 (m, 1H), 5.1–5.4 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 26.1, 26.2, 27.5, 29.0, 30.0, 31.8, 33.4, 36.3, 128.1, 136.0; MS *m/z* (rel intensity): 194 (M^+, 5), 109 (65), 96 (100), 82 (29), 67 (17), 55 (34). Anal. Calcd for $C_{14}H_{26}$: C, 86.52; H, 13.48. Found: C, 86.46; H, 13.57. The *E/Z* ratio was determined by ^1H NMR analysis of the corresponding epoxide.[23] ***cis*-1-Cyclohexyl-1,2-epoxyoctane.** ^1H NMR ($CDCl_3$): δ 0.81 (t, *J*=6.9 Hz, 3H), 0.9–1.5 (m, 12H), 1.3–1.6 (m, 4H), 1.4–1.8 (m, 4H), 1.8–2.0 (m, 1H), 2.55 (dd, *J*=4.0, 8.0 Hz, 1H), 2.8–2.9 (m, 1H).

(*Z*)-2,2-Dimethyl-3-undecene. The title compound was produced by the reduction with either a $NbCl_5$–Zn system (procedure C) or a $TaCl_5$–Zn system (four-fold excess of the low-valent tantalum ($TaCl_5$ (4.0 mmol) and Zn (6.0 mmol)) were employed). Bp 88–90 °C (bath temp, 13 Torr); IR (neat): 2954, 2922, 1729, 1466, 1363, 1273 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.7 Hz, 3H), 1.08 (s, 9H), 1.1–1.5 (m, 10H), 2.0–2.3 (m, 2H), 5.15 (dt, *J*=12.0, 7.0 Hz, 1H), 5.31 (d, *J*=12.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 28.4, 29.3, 29.4, 30.4, 31.2, 31.9, 33.1, 129.1, 139.6; MS *m/z* (rel intensity): 182 (M^+, 3), 139 (3), 97 (20), 83 (100), 69 (69), 55 (48). Anal. Calcd for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.61; H, 14.54. The *E/Z* ratio was determined by ^1H NMR analysis of the corresponding epoxide.[23] ***cis*-2,2-Dimethyl-3,4-epoxyundecane.** ^1H NMR ($CDCl_3$): δ 0.87 (t, *J*=6.8 Hz, 3H), 0.98 (s, 9H), 1.2–1.5 (m, 10H), 1.6–1.9 (m, 2H), 2.63 (d, *J*=4.2 Hz, 1H), 2.8–2.9 (m, 1H). **(*E*)-2,2-Dimethyl-3-undecene.** ^1H NMR ($CDCl_3$): δ 0.92 (t, *J*=6.7 Hz, 3H), 0.99 (s, 9H), 1.2–1.5 (m, 10H), 1.9–2.1 (m, 2H), 5.29 (dt, *J*=15.7, 6.3 Hz, 1H), 5.43 (d, *J*=15.7 Hz, 1H). ***trans*-2,2-Dimethyl-3,4-epoxyundecane.** ^1H NMR ($CDCl_3$): δ 0.81 (t, *J*=6.8 Hz, 3H), 0.85 (s, 9H), 1.1–1.5 (m, 10H), 1.5–1.6 (m, 2H), 2.45 (d, *J*=2.3 Hz, 1H), 2.7–2.8 (m, 1H).

(*Z*)-1-(Trimethylsilyl)-1-dodecene. The title compound was produced by

the reduction with either a $NbCl_5$–Zn system (procedure C) or a $TaCl_5$–Zn system. Bp 76–78 °C (bath temp, 1 Torr); IR (neat): 2922, 2852, 1607, 1466, 1248, 837, 761, 688 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.08 (s, 9H), 0.93 (t, *J*=6.8 Hz, 3H), 1.1–1.5 (m, 16H), 2.0–2.2 (m, 2H), 5.45 (d, *J*=14.0 Hz, 1H), 6.29 (dt, *J*=14.0, 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 0.58, 14.1, 22.7, 29.4, 29.8, 32.0, 33.6, 128.7, 149.3; MS *m/z* (rel intensity) 240 (M^+, 0.8), 225 (50), 114 (27), 73 (100), 59 (61). Anal. Calcd for $C_{15}H_{32}Si$: C, 74.91; H, 13.41. Found: C, 74.48; H, 13.57. The *E/Z* ratio was determined by ^1H NMR analysis. **(*E*)-1-(trimethylsilyl)-1-dodecene.** ^1H NMR ($CDCl_3$): δ 0.02 (s, 9H), 0.85 (t, *J*=6.7 Hz, 3H), 1.1–1.5 (m, 16H), 2.0–2.2 (m, 2H), 5.59 (d, *J*=18.0 Hz, 1H), 6.02 (dt, *J*=18.0, 6.1 Hz, 1H).

(*Z*)-1,6-Undecadiene.[24] The title compound was produced by the reduction with a $TaCl_5$–Zn system. ^1H NMR ($CDCl_3$): δ 0.90 (t, *J*=7.0 Hz, 3H), 1.2–1.4 (m, 4H), 1.46 (dd, *J*=6.9, 7.3 Hz, 2H), 1.9–2.2 (m, 6H), 4.95 (d, *J*=10.3 Hz, 1H), 5.01 (d, *J*=17.0 Hz, 1H), 5.3–5.5 (m, 2H), 5.82 (ddt, *J*=10.3, 17.0, 6.8 Hz, 1H). The *E/Z* ratio was determined by ^1H NMR analysis of the corresponding epoxide.[23] ***cis*-6,7-Epoxy-1-undecene.** ^1H NMR ($CDCl_3$): δ 0.93 (t, *J*=6.8 Hz, 3H), 1.2–1.8 (m, 10H), 2.0–2.3 (m, 2H), 2.9–3.0 (m, 2H), 4,98 (d, *J*=17.1 Hz, 1H), 5.01 (d, *J*=10.3 Hz, 1H), 5.82 (ddt, *J*=10.3, 17.1, 6.6 Hz, 1H).

(*Z*)-1,8-Octadecadiene. The title compound was produced by the reduction with a $TaCl_5$–Zn system. Bp 103–105 °C (bath temp, 0.20 Torr); IR (neat): 2922, 2852, 1735, 1642, 1460, 1271, 991 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.9 Hz, 3H), 1.2–1.5 (m, 16H), 1.3–1.5 (m, 4H), 1.9–2.2 (m, 6H), 4.95 (d, *J*=10.3 Hz, 1H), 5.00 (d, *J*=16.9 Hz, 1H), 5.3–5.5 (m, 2H), 5.82 (ddt, *J*=10.3, 16.9, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 27.0, 27.2, 28.6, 29.2, 29.4, 29.6, 29.7, 29.8, 31.9, 33.7, 114.2, 129.6, 130.1, 139.0; MS *m/z* (rel intensity): 250 (M^+, 4), 123 (9), 96 (75), 82 (100), 67 (76), 55 (79). Anal. Calcd for $C_{18}H_{34}$: C, 86.32; H, 13.68. Found: C, 86.18; H, 13.61. The *E/Z* ratio was determined by ^1H NMR analysis of

the corresponding epoxide.[23] ***cis*-7,8-Epoxy-1-octadecene.** ^{1}H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.8 Hz, 3H), 1.2–1.5 (m, 14H), 1.3–1.6 (m, 10H), 2.0–2.1 (m, 2H), 2.9–3.0 (m, 2H), 4.95 (d, *J*=10.2 Hz, 1H), 5.01 (d, *J*=17.1 Hz, 1H), 5.81 (ddt, *J*=10.2, 17.1, 6.6 Hz, 1H).

(*Z*)-5-Octadecen-1-ol. The title compound was produced by the reduction with a $TaCl_5$–Zn system: Bp 146–147 °C (bath temp, 0.30 Torr); IR (neat): 3318, 2922, 2850, 1652, 1466, 1067 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.8 Hz, 3H), 1.1–1.5 (m, 21H), 1.4–1.5 (m, 2H), 1.5–1.7 (m, 2H), 1.9–2.2 (m, 4H), 3.6–3.7 (m, 2H), 5.3–5.5 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 14.2, 22.7, 25.9, 26.9, 27.3, 29.4, 29.6, 29.7, 31.9, 32.4, 62.9, 129.3, 130.4; MS *m/z* (rel intensity): 250 (M^+-H_2O, 6), 123 (10) 96 (58), 82 (100), 41 (66). Anal. Calcd for $C_{18}H_{36}O$: C, 80.53; H, 13.52. Found: C, 80.56; H, 13.63. The *E*/*Z* ratio was determined by ^{1}H NMR analysis of the epoxide of the *tert*-butyldimethylsilyl ether of the alcohol.[23] ***cis*-5,6-Epoxy-1-(*tert*-butyldimethylsiloxy)-octadecane.** ^{1}H NMR ($CDCl_3$): δ 0.03 (s, 6H), 0.86 (s, 12H), 1.2–1.4 (m, 16H), 1.4–1.8 (m, 12H), 2.9–3.0 (m, 2H), 3.62 (t, *J*=5.9 Hz, 2H).

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(11) A mixture of $NbCl_5$ (4.0 equiv) and aluminum powder (6.0 equiv) in DME–benzene after ultrasonic irradiation shows dark orange color.

(12) Treatment of 6–dodecyne with 2 equiv of the $NbCl_5$–Zn reagent in DME–benzene (1:1) at 25 °C for 18 h gave 6–dodecene in 52% yield along with 18% of the starting alkyne. When 4 equiv of $NbCl_5$ was employed, the reduction of 6–dodecyne was completed in 5.5 h (80% yield).

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(15) Aldehydes and ketones were converted into the pinacol–type 1,2–diols with the low–valent tantalum (or niobium). For example, treatment of 3–phenylpropanal and cyclohexanone with the $TaCl_5$–Zn reagent in DME–benzene at 25 °C for 10 min afforded the corresponding 1,2–diols in 99% and 82% yields, respectively. Cinnamyl alcohol dimerized with loss of the hydroxyl group to afford a mixture of 1,5–dienes in 73% yield by the action of the low–valent tantalum. See also ref 2.

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CHAPTER 3

Regio- and Stereoselective Synthesis of Allylic Alcohols Mediated by Tantalum-Alkyne Complexes.

A variety of tantalum-alkyne complexes are generated *in situ* by treatment of alkynes with low-valent tantalum derived from $TaCl_5$ and zinc. These complexes add regioselectively to carbonyl compounds in a one-to-one fashion to yield (*E*)-allylic alcohols stereoselectively. Iodinolysis of the oxatantalacyclopentene, which is postulated as an intermediate of the reaction, gives a (*Z*)-3-iodo-2-propen-1-ol derivative. In the case of α,β-unsaturated aldehydes, reaction of oxatantalacyclopentene with the aldehyde takes place at the *cis* vicinal alkene positions and one-to-two addition products of the tantalum-alkyne complexes and aldehydes are obtained.

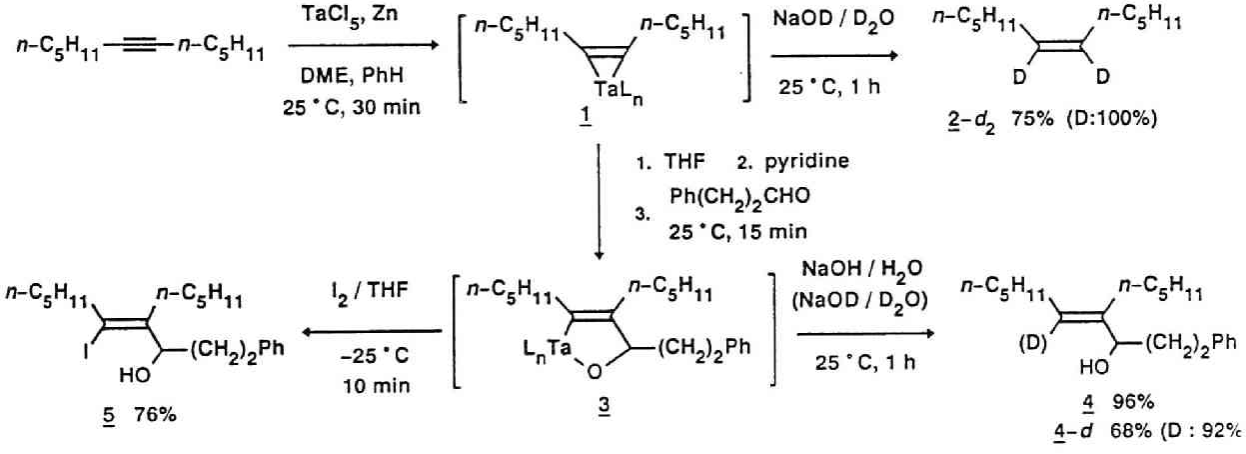
Since the discovery of transition metal–alkyne complexes, many reports on their structure and reactivities have appeared.[1-12] Recently, they received much attention as useful intermediates in organic synthesis. One of the leap in synthetic chemistry using metal–alkyne complexes is cyclotrimerization of alkynes with cobalt catalysis.[1a,b,c] Titanocene–[2] and zirconocene–alkyne complexes[3] are also employed in carbon–carbon bond formation. In contrast, group 5 metal–alkyne complexes have not been widely utilized in organic synthesis until quite recently.[4a,b,5] Low–valent tantalum complexes react with inactivated acetylenic triple bonds to form tantalum–alkyne complexes.[5,6,7] The isolated tantalum–alkyne complexes are sterically congested, and the only carbon–carbon bond forming transformations which have been effected using these complexes are cyclotrimerizations[6] and coupling reactions with nitriles.[7f] We disclose herein (i) that the tantalum–alkyne complexes, which are generated *in situ* by treatment of alkynes with low–valent tantalum, are reacted in a one–to–one fashion with carbonyl compounds to yield (*E*)–allylic alcohols in a regio– and stereoselective manner, and (ii) that they react with two equiv of carbonyl compounds at *cis* vicinal positions of the alkenes in the case of α,β–unsaturated aldehydes.

Reaction of Tantalum–Alkyne Complexes with Saturated Carbonyl Compounds[5c]

A variety of tantalum–alkyne complexes have been generated *in situ* by treatment of alkynes with low–valent tantalum derived from $TaCl_5$ and zinc in a mixed solvent of DME and benzene (see Chapter 2). Although the structure of the tantalum–alkyne complexes is not characterized, treatment of the complexes with a NaOD–D_2O solution gave the corresponding *cis* vicinal dideuterated alkenes. The

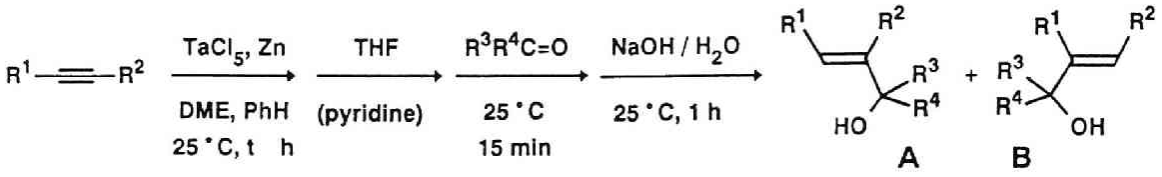
result prompted us to examine the use of the tantalum–alkyne complexes as a *cis* vicinal alkene dianion synthon.[4b,5] Treatment of tantalum–6–dodecyne complex **1** with 3–phenylpropanal at 25 °C for 20 min afforded the allylic alcohol **4** in 96% yield after aqueous alkaline workup (Scheme I). The tantalum complex **1** did not reacted with another 3–phenylpropanal and one–to–two addition product of **1** and 3–phenylpropanal was not observed even in the presence of excess amounts of aldehyde (*vide infra*). (*E*)–Allylic alcohol was produced exclusively,[13] as expected from the insertion of a carbonyl group into the tantalum–carbon bond of the complex **1**.

Scheme 1



The results of the preparation of allylic alcohols from alkynes and carbonyl compounds are summarized in Table 1.

Table 1. Synthesis of Allylic Alcohols from Alkynes and Carbonyl compounds.[a]



Run	R^1	R^2	R^3	R^4	t / h	Yield/%[b]	**A / B**[c]
1	n-C_5H_{11}	n-C_5H_{11}	Ph	H	0.5	85	--
2			n-C_8H_{17}	H	0.5	94	--
3			$Ph(CH_2)_2$	H	0.5	96	--
4			c-C_6H_{11}	H	0.5	87	--
5			t-Bu	H	0.5	82	--
6			$-(CH_2)_5-$		0.5	87	--
7			c-C_6H_{11}	n-C_6H_{13}	0.5	41[d]	--
8			c-C_6H_{11}	c-C_6H_{11}	0.5	trace[e]	--
9	n-$C_{10}H_{21}$	H	n-C_8H_{17}	H	0.7	48[f]	>99 / <1
10			$-(CH_2)_5-$		0.7	45[f]	>99 / <1
11	c-C_6H_{11}	n-C_6H_{13}	$Ph(CH_2)_2$	H	1.5	80	65 / 35
12			$-(CH_2)_5-$		1.5	83	76 / 24
13	t-Bu	n-C_7H_{15} (**6**)	$Ph(CH_2)_2$	H	4.5	67[g,h]	>99 / <1
14			$-(CH_2)_5-$		4.5	<5[g,i]	--
15	n-C_6H_{13}	Ph (**7**)	$Ph(CH_2)_2$	H	1	73	83 / 17
16			$-(CH_2)_5-$		1	80	79 / 21
17	Me_3Si	n-$C_{10}H_{21}$	$Ph(CH_2)_2$	H	1.5	77[j]	89 / 11

18			$-(CH_2)_5-$		1.5	85[j]	>99 / <1
19	Me_3Si	Ph	$Ph(CH_2)_2$	H	3	71[g,j]	>99 / <1
20	t-$BuMe_2Si$	n-$C_{10}H_{21}$	$Ph(CH_2)_2$	H	3	68[g,j]	>99 / <1
21			$-(CH_2)_5-$		3	71[g,j]	>99 / <1

a) $TaCl_5$ (2.0 equiv), zinc (3.0 equiv), and pyridine (4.0 equiv) were employed. Tantalum–alkyne complex was treated with a carbonyl compound (1.2 equiv) at 25°C for 15 min. b) Isolated yields. c) The isomer ratios were determined by ^1H NMR analysis. d) Unreacted 6–dodecene was recovered in 46% yield. e) 6–Dodecene was recovered in 91% yield. f) $TaCl_5$ (1.0 equiv), zinc (1.5 equiv), and pyridine (2.0 equiv) were employed. Tantalum–1–dodecyne complex was treated with a carbonyl compound (1.2 equiv) at 25 °C for 45 min. g) $TaCl_5$ (4.0 equiv), zinc (6.0 equiv) and pyridine (8.0 equiv) were employed. h) (*Z*)–2,2–Dimethyl–3–undecene was obtained in 24% yield. i) The unreacted olefin was recovered in 81% yield. Cyclohexanone was recovered in 32% yield and the pinacol–type 1,2–diol of cyclohexanone was produced in 45% yield. j) The reaction was conducted without addition of pyridine.

Yields of allylic alcohols depended on additives prior to addition of an aldehyde. Coupling reactions between tantalum–alkyne complexes and aldehydes without addition of THF was marginal, and many by–products appeared. Pretreatment of the complexes with pyridine was essential to suppress the formation of 1,3–dienes through dehydration of the allylic alcohols, especially in the case of ketones. Tantalum–6–dodecyne complex **1** reacted with pivalaldehyde (run 5), whereas sterically hindered dicyclohexyl ketone did not react with **1**, and unreacted 6–dodecene was recovered in 91% yield (run 8).

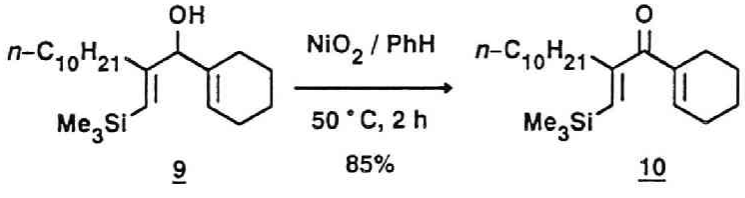
In the case of unsymmetrical alkynes, two regioisomeric adducts could be produced. The regioselectivities (**A/B**) of the reactions with the tantalum–alkyne complexes are higher than those observed with zirconocene–alkyne complexes.[3b,3e] Bulkiness of the substituents R^1, R^2, R^3, and R^4 influences the regiochemistry of the products. Thus, as R^1, R^3, or R^4 become bigger, or as R^2 becomes smaller, higher regioselectivities (**A/B**) are obtained (except runs 15 and 16). In the case of the sterically crowded alkyne **6**, both reactions, reduction of the acetylenic bond and addition of the tantalum–alkyne complex to carbonyl compounds, were retarded (runs 13 and 14). The results of the reactions between the aromatic alkyne **7** and carbonyl compounds reveal that electronic effects are also directing factors of the regiochemistry (runs 15 and 16). In the case of terminal alkynes, significant amounts (ca. 40% yield) of polymeric products were obtained as by–products, but this did not involve cyclotrimerized aromatic compounds (runs 9 and 10).[4a,6]

As shown in scheme 1, quenching of the reaction mixture with $NaOD/D_2O$ gave monodeuterated alcohol **4–*d*** in 68% yield. This observation suggests the formation of an oxatantalacyclopentene **3** as an intermediate. The oxatantalacyclopentene **3** could be trapped with I_2 at −25 °C to give iodo alcohol **5** in 76% yield (Scheme 1).

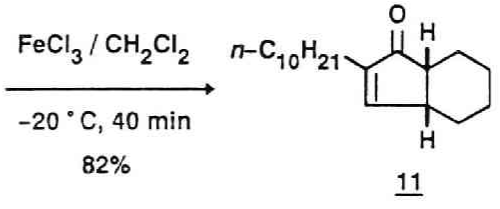
Reaction of Tantalum-Alkyne Complexes with α,β-Unsaturated Carbonyl Compounds

Reaction of tantalum-6-dodecyne complex **1** with acrolein at 25°C for 15 min produced (*E*)-4-pentyl-1,4-decadien-3-ol (**8**) in 60% yield along with a regioisomeric mixture of trienes derived by dehydration of the dienol **8** in 12% yield. The yield of **8** was improved when reaction was conducted at 0 °C and 2.0 equiv of acrolein was employed. Other results between tantalum-alkyne complexes and α,β-unsaturated carbonyl compounds are summarized in Table 2. (*E*)-Allylic alcohols were produced stereoselectively. The regioselectivities (**A/B**) of the addition varies with the bulkiness of the substituents, similarly to the reactions between tantalum-alkyne complexes and saturated carbonyl compounds.

1-(Trimethylsilyl)-substituted 1,4-dien-3-ol is a useful precursor for silicon-directed Nazarov cyclization (eq 1).[14] Oxidation of dienol **9**, derived by reaction of a tantalum-(1-(trimethylsilyl)-1-dodecyne) complex and 1-cyclohexenyl-carbaldehyde (Table 2, run 9), was performed with nickel peroxide.[15] Nazarov cyclization of divinyl ketone **10** at -20 °C with $FeCl_3$ afforded bicyclo[4.3.0]nonene derivative **11** in 82% yield.[14]

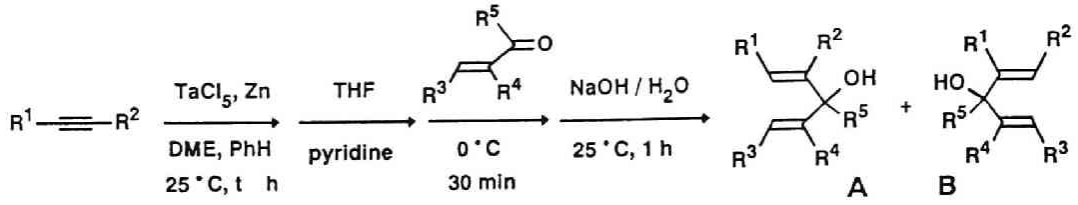


9 10



11 (1)

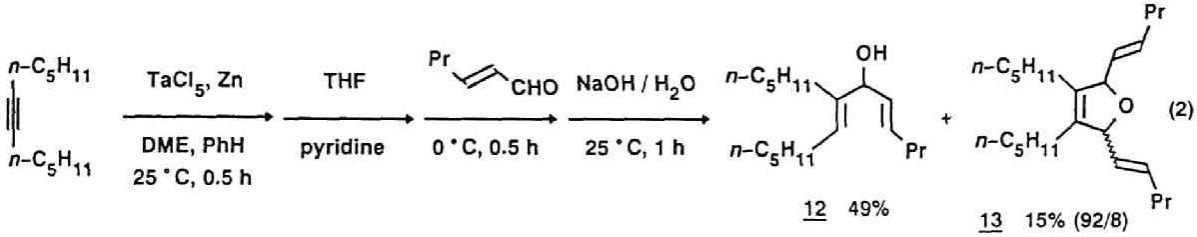
Table 2. Reactions between Tantalum–Alkyne Complexes and α,β-Unsaturated Carbonyl Compounds.[a]



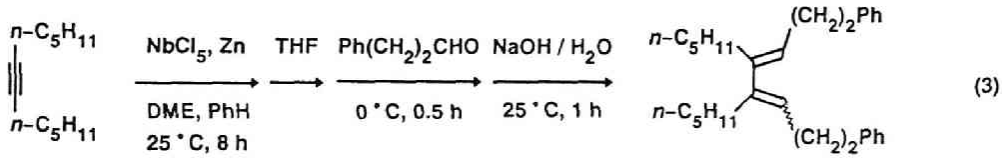
Run	R^1	R^2	R^3	R^4	R^5	t / h	Yield/%[b]	**A / B**[c]
1	n-C_5H_{11}	n-C_5H_{11}	H	H	H	0.5	78	--
2						0.5	60[d]	--
3			H	Me	H	0.5	85	--
4			H	H	Me	0.5	76	--
5	n-C_6H_{13}	Ph	H	H	H	1.5	75	71 / 29
6			H	H	Me	1.5	73	71 / 29
7	Me_3Si	n-$C_{10}H_{21}$	H	H	H	2	82[e]	97 / 3
8			H	H	Me	2	85[e]	>99 / <1
9			-(CH_2)-		H	2	81[e]	>99 / <1
10			Pr	H	H	2	71[e]	>99 / <1
11	t-$BuMe_2Si$	n-$C_{10}H_{21}$	H	H	H	4	75[f]	>99 / <1

a) $TaCl_5$ (2.0 equiv), zinc (3.0 equiv), and pyridine (4.0 equiv) were employed. Tantalum–alkyne complex was treated with α,β-unsaturated carbonyl compound (2.0 equiv) at 0°C for 30 min. b) Isolated yields. c) The ratio was determined by ^1H NMR analysis. d) The reaction was conducted at 25 °C with 1.2 equiv of acrolein (see the text). e) $TaCl_5$ (2.0 equiv), zinc (3.0 equiv), and pyridine (2.0 equiv) were employed. f) $TaCl_5$ (4.0 equiv), zinc (6.0 equiv), and pyridine (4.0 equiv) were employed.

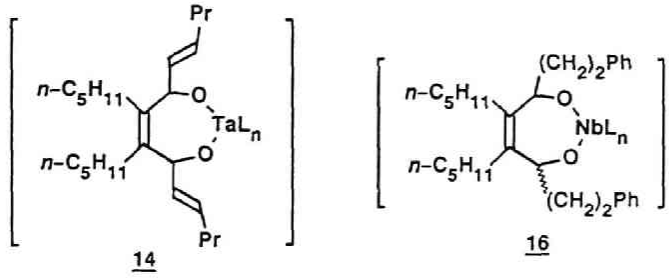
It is interesting to note that considerable amounts of one-to-two addition products of tantalum-alkyne complexes and aldehydes were produced in the case of α,β-unsaturated aldehydes having one β-substituent. For example, treatment of a tantalum-6-dodecyne complex with 2-hexenal at 0 °C for 30 min produced the allylic alcohol **12** in 49% yield and two stereoisomers of 2,5-dihydrofuran derivatives **13** in 15% yield (eq 2).



(2)



(3)

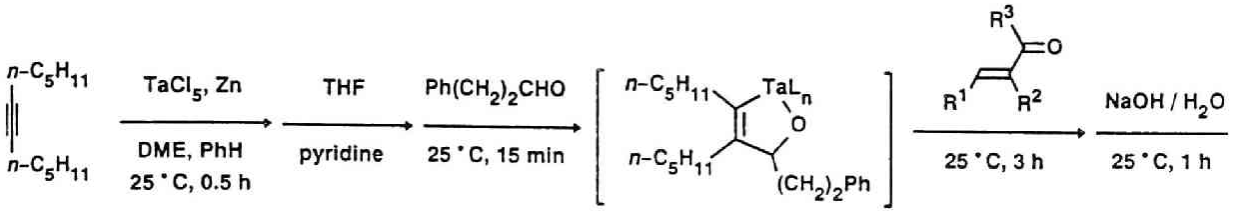


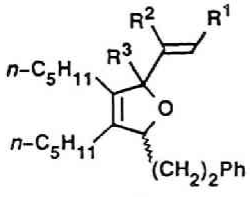
Analogous one-to-two addition reactions of metal-alkyne complexes with aldehydes have been observed in the case of niobium-alkyne complexes.[16] Treatment of a niobium-1-dodecyne complex with 2 equiv of 3-phenylpropanal afforded *E* and *Z* mixture of 1,3-dienes **15** *via* dioxaniobacycloheptene **16** (eq 3).[17] In contrast to the niobium case, reaction of a tantalum-alkyne complex with a β-substituted α,β-unsaturated aldehyde produces 2,5-dihydrofuran derivatives

through uptake of one oxygen from dioxatantalacycloheptene **14**. Oxatantalacyclopentene does not react with saturated aldehydes even in the presence of the excess a mounts of the aldehydes (*vide supra*). To examine the reactivity of the oxatantalacyclopentene toward α,β–unsaturated aldehydes, α,β–unsaturated aldehydes were added as a second component to the reaction mixture of tantalum–6–dodecyne complex and 3–phenylpropanal (Table 3).

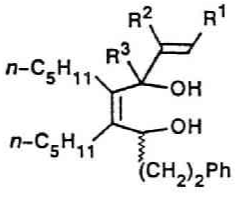
Reactions were conducted at 25°C and the following four compounds **C**, **D**, **E**, and **F** were produced. One–to–two adducts, **C**, **D**, and **E** were produced in all cases except α,β–unsaturated ketone (run 4). 2,5–Dihydrofuran derivatives were produced especially in the case of the aldehyde having a β–substituent. It is, however, still obscure why β–substituent is required for the formation of 2,5–dihydrofurans.

Table 3. Reactions of Oxatantalacyclopentene, Derived from a Tantalum-6-Dodecyne Complex and 3-Phenylpropanal, with α,β-Unsaturated Compounds.[a]

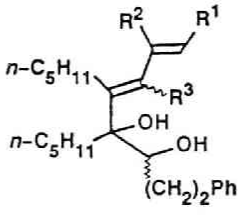




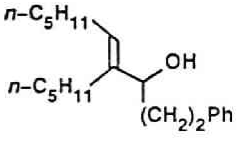
C



D



E



F

Run	R^1	R^2	R^3	Yields/%[b]			1 to 2 Adducts	Yield/%
				C	D	E		F
1	H	H	H	0	6[c]	21[d]	(27)	44
2	Pr	H	H	46[e]	<1	23[f]	(69)	0
3	H	Me	H	<1	38[g]	28[h]	(66)	19
4	$-(CH_2)_4-$		Me	0	<1	<1	(<1)	79

a) $TaCl_5$ (2.0 equiv), zinc (3.0 equiv), and pyridine (4.0 equiv) were employed. To the tantalum-alkyne complex was added 3-phenylpropanal (1.2 equiv) and the mixture was stirred at 25°C for 15 min and then the mixture was treated with α,β-unsaturated carbonyl compound (2.0 equiv) at 25°C for 3 h. b) Isolated yields. c) Two diastereomers were produced (major/minor=80/20). d) Major/minor=57/43. e) Major/minor=70/30. f) Major/minor=65/35. g) Major/minor=79/21. h) Major/minor=78/22.

Experimental Section

Preparation of Internal Alkynes. Internal alkynes were prepared according to the standard procedure described in ref. 18.

1-(*tert*-Butyldimethylsilyl)-1-dodecyne. To a stirred solution of 1-dodecyne (4.2 g, 25 mmol) in THF (25 mL) at 0 °C under an argon atmosphere was added butyllithium (16 mL of a 1.6 M hexane solution, 25 mmol) dropwise over a period of 10 min. After the reaction mixture was stirred at 0 °C for 15 min, *tert*-butylchlorodimethylsilane (3.8 g, 25 mmol) was added to the mixture; the resulting mixture was stirred at 0 °C for an additional 1h. The mixture was poured into ice-cold water and extracted with hexane. The organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Distillation of the crude product gave 6.7 g (96%) of 1-(*tert*-butyldimethylsilyl)-1-dodecyne. Bp 118-120 °C (0.20 Torr); IR (neat): 2924, 2854, 2170, 1730, 1464, 1249, 837, 773 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.08 (s, 6H), 0.91 (t, *J*=6.4 Hz, 3H), 0.93 (s, 9H), 1.0-1.4 (m, 14H), 1.4-1.6 (m, 2H), 2.1-2.3 (m, 2H); ^{13}C NMR ($CDCl_3$): δ -4.4, 14.1, 16.6, 19.8, 22.7, 26.1, 28.7, 28.8, 29.1, 29.4, 29.6, 31.9, 82.3, 108.2; MS *m/z* (rel intensity): 280 (M^+, 1), 223 (100), 125 (5), 73 (26), 59 (42). Anal. Calcd for $C_{18}H_{36}Si$: C, 77.06; H, 12.93. Found: C, 76.80; H, 12.99.

2-Phenyl-1-(trimethylsilyl)-1-ethyne.[19] The title compound was prepared in 89 % yield from phenylacetylene and chlorotrimethylsilane. ^1H NMR ($CDCl_3$): δ 0.25 (s, 9H), 7.2-7.4 (m, 3H), 7.4-7.6 (m, 2H).

General Procedure for the Synthesis of Allylic Alcohols from Alkynes and Saturated Carbonyl Compounds. In a 50-mL reaction flask was placed $TaCl_5$ (0.72 g, 2.0 mmol) under an argon atmosphere. To the salt were added at 25 °C benzene (5 mL) and DME (5 mL) successively. Zinc dust (0.20 g, 3.0 mmol) was added at 25 °C to a stirred pale yellow solution of $TaCl_5$, and the mixture was

stirred at 25 °C for 40 min. The color of the mixture turned to greenish dark blue with slightly exothermic process. To the mixture was added at 25 °C a solution of an alkyne (1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C. After consumption of the alkyne was confirmed by TLC, THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added to the mixture; the resulting mixture was stirred at 25 °C for an additional 15 min. A saturated carbonyl compound (1.2 mmol) was added to the mixture at 25 °C, and the mixture was stirred at 25 °C for 15 min. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed well with ethyl acetate (3x5 mL). Organic extracts were concentrated *in vacuo* and diluted with hexane (10 mL), dried over $MgSO_4$, and concentrated again *in vacuo*. Purification of the crude product by column chromatography on silica gel gave the desired allylic alcohol.

(*E*)-2-Pentyl-1-phenyl-2-octen-1-ol. Bp 131-133 °C (bath temp, 0.14 Torr); IR (neat): 3344, 2952, 2924, 2856, 1491, 1465, 1378, 1006, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.83 (t, *J*=6.9 Hz, 3H), 0.90 (t, *J*=6.9 Hz, 3H), 1.1-1.5 (m, 12H), 1.76 (d, *J*=3.5 Hz, 1H), 1.7-2.1 (m, 2H), 2.0-2.2 (m, 2H), 5.15 (d, *J*=3.5 Hz, 1H), 5.61 (t, *J*=7.2 Hz, 1H), 7.2-7.5 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.8, 14.9, 23.2, 23.4, 28.4, 28.5, 29.9, 30.3, 32.5, 33.0, 78.8, 127.3, 128.0, 129.9, 142.1, 143.6; MS *m/z* (rel intensity): 274 (M^+, 27), 203 (100), 133 (46), 105 (53), 77 (19). Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.00; H, 11.23.

(*E*)-7-Pentyl-6-hexadecen-8-ol. Bp 113-115 °C (bath temp, 0.12 Torr); IR (neat): 3340, 2954, 2924, 2852, 1466, 1379, 1052, 1013, 723 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8-1.1 (m, 9H), 1.2-1.5 (m, 25H), 1.4-1.6 (m, 2H), 1.9-2.1 (m, 4H), 3.9-4.1 (m, 1H), 5.37 (t, *J*=7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.5, 22.6, 22.7, 26.0, 27.5, 29.3, 29.5, 29.6, 29.8, 31.6, 31.9, 32.4, 35.7, 76.9, 126.8, 140.1;

MS *m/z* (rel intensity): 310 (M^+, 4), 239 (69), 197 (100), 71 (61), 43 (44). Anal. Calcd for $C_{21}H_{42}O$: C, 81.22; H, 13.63. Found: C, 81.02; H, 13.87.

(*E*)-4-Pentyl-1-phenyl-4-decen-3-ol (4). Bp 140–143 °C (bath temp, 0.20 Torr); IR (neat): 3348, 2952, 2924, 2856, 1604, 1496, 1456, 1048, 746, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.2–1.5 (m, 13H), 1.85 (ddd, *J*=6.7, 7.9, 7.9 Hz, 2H), 1.9–2.2 (m, 4H), 2.60 (dt, *J*=14.0, 7.9 Hz, 1H), 2.73 (dt, *J*=14.0, 7.9 Hz, 1H), 4.0–4.1 (m, 1H), 5.40 (t, *J*=7.3 Hz, 1H), 7.2–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.9, 23.3, 23.4, 28.3, 30.4, 30.5, 32.5, 33.1, 33.2, 38.2, 76.8, 126.5, 127.8, 129.1, 129.2, 142.6, 143.0; MS *m/z* (rel intensity): 302 (M^+, 65), 231 (99), 197 (100), 71 (9). Anal. Calcd for $C_{21}H_{34}O$: C, 83.38; H, 11.33. Found: C, 83.12; H, 11.46.

(*E*)-1-Cyclohexyl-2-pentyl-2-octen-1-ol. Bp 127–129 °C (bath temp, 0.14 Torr); IR (neat): 3382, 2922, 2850, 1658, 1466, 1450, 1382, 1000 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.1 (m, 6H), 1.0–1.6 (m, 20H), 1.6–1.9 (m, 4H), 1.9–2.2 (m, 4H), 3.6–3.8 (m, 1H), 5.32 (t, *J*=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 17.5, 23.2, 26.8, 26.9, 27.3, 28.2, 28.5, 29.5, 30.3, 30.6, 30.8, 32.4, 33.2, 42.0, 82.9, 128.7, 141.6; MS *m/z* (rel intensity): 280 (M^+, 2), 209 (9), 197 (100), 83 (23), 71 (56). Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.20; H, 13.16.

(*E*)-2,2-Dimethyl-4-pentyl-4-decen-3-ol. Bp 103–105 °C (bath temp, 0.34 Torr); IR (neat): 3482, 2954, 2926, 2858, 1466, 1362, 1002 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 0.91 (s, 9H), 1.2–1.5 (m, 13H), 1.7–1.9 (m, 1H), 1.9–2.2 (m, 2H), 2.1–2.4 (m, 1H), 3.75 (d, *J*=2.2 Hz, 1H), 5.39 (t, *J*=7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 26.4, 27.6, 29.6, 29.8, 30.6, 31.6, 32.3, 35.9, 82.6, 127.9, 141.8; MS *m/z* (rel intensity): 254 (M^+, 0.4), 197 (100), 71 (76), 57 (39). Anal. Calcd for $C_{17}H_{34}O$: C, 80.24; H, 13.47. Found: C, 80.10; H, 13.42.

(*E*)-1-(1-Pentyl-1-heptenyl)cyclohexanol. Bp 122–124 °C (bath temp, 0.14 Torr); IR (neat): 3402, 2926, 2854, 1467, 1459, 1449, 1378, 1149, 955 cm^{-1};

^{1}H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.1–1.5 (m, 13H), 1.5–1.8 (m, 10H), 1.9–2.1 (m, 4H), 5.47 (t, *J*=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.8, 22.9, 23.2, 23.4, 26.4, 28.5, 28.7, 30.4, 31.3, 32.3, 32.4, 33.4, 37.2, 78.4, 124.8, 146.7; MS *m/z* (rel intensity): 266 (M^+, 15), 223 (13), 195 (100), 55 (30), 43 (27). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.23; H, 13.11.

(*E*)-7-Cyclohexyl-8-pentyl-8-tetradecen-7-ol. Bp 137–139 °C (bath temp, 0.20 Torr); IR (neat): 3500, 2922, 2852, 1466, 1340, 1270, 1120, 1071, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.8–1.1 (m, 9H), 1.0–1.6 (m, 28H), 1.4–1.9 (m, 4H), 1.7–2.0 (m, 4H), 2.0–2.2 (m, 2H), 5.26 (t, *J*=7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.5, 22.7, 23.7, 26.7, 26.8, 27.0, 27.4, 27.9, 28.6, 29.3, 29.8, 29.9, 31.7, 31.9, 32.8, 36.7, 45.1, 80.2, 125.4, 141.6; MS *m/z* (rel intensity): 281 ($M^+-C_6H_{11}$, 100), 113 (7), 83 (12), 71 (3). Anal. Calcd for $C_{25}H_{48}O$: C, 82.34; H, 13.27. Found: C, 82.04; H, 13.27.

(*E*)-10-Henicosen-9-ol. $TaCl_5$ (1.0 equiv), zinc (1.5 equiv), and pyridine (2.0 equiv) were employed. Bp 145–147 °C (bath temp, 0.12 Torr); IR (neat): 3314, 2922, 2850, 1669, 1467, 1378, 1147, 1086, 1055, 1035, 968, 720, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.5 Hz, 6H), 1.1–1.7 (m, 31H), 2.02 (dt, *J*=6.4, 6.6 Hz, 2H), 4.0–4.1 (m, 1H), 5.44 (dd, *J*=7.0, 15.4 Hz, 1H), 5.64 (dt, *J*=15.4, 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.8, 23.4, 26.2, 29.9, 30.0, 30.1, 30.2, 30.3, 30.4, 32.6, 32.9, 38.1, 73.8, 132.7, 133.9; MS *m/z* (rel intensity): 292 (M^+-H_2O, 13), 197 (75), 169 (29), 95 (77), 57 (100). Anal. Calcd for $C_{21}H_{42}O$: C, 81.22; H, 13.63. Found: C, 81.02; H, 13.85.

(*E*)-1-Dodecenylcyclohexanol. $TaCl_5$ (1.0 equiv), zinc (1.5 equiv), and pyridine (2.0 equiv) were employed. Bp 117–119 °C (bath temp, 0.12 Torr); IR (neat): 3364, 2922, 2852, 1449, 1055, 1034, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.8–1.0 (m, 3H), 1.1–1.5 (m, 17H), 1.3–1.7 (m, 10H), 1.9–2.1 (m, 2H), 5.62 (d, *J*=15.6 Hz, 1H), and 5.66 (dt, *J*=15.6, 5.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.8, 22.9, 23.3,

26.3, 29.8, 30.0, 30.1, 30.3, 32.6, 33.0, 38.8, 71.9, 128.8, 138.3; MS *m/z* (rel intensity): 266 (M^+, 24), 223 (45), 125 (100), 83 (35), 57 (13). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.26; H, 12.84.

(*E*)-1-Cyclohexyl-2-hexyl-5-phenyl-1-penten-3-ol (A) and (*E*)-4-Cyclohexyl-1-phenyl-4-undecen-3-ol (B). The regioisomer ratio was determined by ^1H NMR analysis (**A**/**B**=65/35). Bp 147–149 °C (bath temp, 0.20 Torr); IR (neat, mixture of **A**/**B**=65/35): 3340, 2922, 2850, 1601, 1496, 1449, 1048, 1031, 896, 745, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.1 (m, 3H), 1.0–1.5 (m, 14H), 1.5–1.9 (m, 7H), 1.9–2.4 (m, 3H), 2.5–2.9 (m, 2H), 4.0–4.2 (m, 1H), 5.23 (d, *J*=9.4 Hz, 1H (**A**)), 5.45 (t, *J*=7.3 Hz, 1H (**B**)), 7.1–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 25.9, 26.0, 26.1, 26.9, 27.6, 29.0, 29.8, 30.0, 30.5, 31.6, 31.7, 32.2, 32.6, 33.3, 33.4, 36.6, 37.3, 38.4, 39.0, 73.0 (**B**), 75.8 (**A**), 125.6, 126.1, 128.2, 128.4, 132.9, 139.8 (**A**), 142.2 (**B**), 142.3 (**A**), 146.6 (**B**); MS *m/z* (rel intensity): 328 (M^+, 5), 245 (44), 219 (38), 105 (21), 91 (100). Anal. Calcd for $C_{23}H_{36}O$: C, 84.09; H, 11.05. Found: C, 84.29; H, 11.06.

(*E*)-1-(2-Cyclohexyl-1-hexylethenyl)cyclohexanol (A) and (*E*)-1-(1-Cyclohexyl-1-octenyl)cyclohexanol (B). The regioisomer ratio was determined by ^1H NMR analysis (**A**/**B**=76/24). Bp 135–137 °C (bath temp, 0.22 Torr); IR (neat, mixture of **A**/**B**=76/24): 3434, 2924, 2850, 1448, 1150, 968, 894cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 3H), 1.0–1.5 (m, 15H), 1.4–1.9 (m, 14H), 1.9–2.3 (m, 3H), 5.29 (d, *J*=10.0 Hz, 1H (**A**)), 5.42 (t, *J*=7.6 Hz, 1H (**B**)); ^{13}C NMR ($CDCl_3$): δ 13.9, 14.1, 22.1, 22.4, 22.6, 22.7, 23.5, 25.7, 26.1, 26.3, 27.5, 27.8, 28.8, 29.1, 29.2, 30.1, 30.5, 31.6, 31.7, 31.8, 32.0, 32.7, 33.5, 34.0, 35.7, 36.5, 37.1, 39.5, 74.1 (**A**), 75.0 (**B**), 124.0 (**B**), 129.9 (**A**), 144.1 (**A**), 149.0 (**B**); MS *m/z* (rel intensity): 292 (M^+, 15), 274 (28), 221(71), 189 (100), 55 (41). Anal. Calcd for $C_{20}H_{36}O$: C, 82.12; H, 12.40. Found: C, 82.36; H, 12.62.

(*E*)-6,6-Dimethyl-4-heptyl-1-phenyl-4-hepten-3-ol. $TaCl_5$ (4.0 equiv),

zinc (6.0 equiv), and pyridine (4.0 equiv) were employed. Bp 133–135 °C (bath temp, 0.18 Torr); IR (neat): 3358, 2952, 2924, 2856, 1604, 1467, 1362, 1096, 745, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 3H), 1.02 (s, 1H), 1.12 (s, 9H), 1.2–1.6 (m, 10H), 1.84 (ddd, *J*=6.8, 8.0, 8.0 Hz, 2H), 1.9–2.1 (m, 1H), 2.1–2.3 (m, 1H), 2.60 (dt, *J*=14.0 8.0 Hz, 1H), 2.74 (dt, *J*=14.0 and 8.0 Hz, 1H), 3.9–4.1 (m, 1H), 5.42 (s, 1H), 6.8–7.1 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 28.3, 29.1, 30.4, 30.6, 31.3, 31.8, 32.4, 32.5, 37.9, 76.8, 125.6, 128.2, 128.4, 136.2, 140.9, 142.2; MS *m/z* (rel intensity): 316 (M^+, 3), 259 (89), 211 (48), 91 (100), 55 (28). Anal. Calcd for $C_{22}H_{36}O$: C, 83.48; H, 11.46. Found: C, 83.19; H, 11.53.

(*E*)-1,4-Diphenyl-4-undecen-3-ol (A) and **(*E*)-1,5-Diphenyl-2-hexyl-1-penten-3-ol (B).** The regioisomer ratio was determined by ^1H NMR analysis (**A**/**B**=83/17). Bp 159–161 °C (bath temp, 0.18 Torr); IR (neat, mixture of **A**/**B**=83/17): 3340, 2950, 2924, 2852, 1602, 1495, 1454, 1071, 747cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 3H), 1.1–1.5 (m, 8H), 1.5–1.6 (m, 1H), 1.7–2.1 (m, 4H), 2.1–2.5 (m, 2H (**B**)), 2.6–2.8 (m, 2H (**A**)), 4.2–4.4 (m, 1H (**B**)), 4.3–4.4 (m, 1H (**A**)), 5.70 (t, *J*=7.4 Hz, 1H (**A**)), 6.54 (s, 1H (**B**)), 7.1–7.5 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 14.2, 22.5, 28.4, 28.8, 29.0, 29.6, 29.7, 31.4, 31.6, 31.9, 32.2, 37.1, 37.5, 75.4 (**B**), 75.9 (**A**), 125.4 (**B**), 125.6 (**A**), 125.7 (**B**), 126.3 (**B**), 126.8 (**A**), 128.0 (**A**), 128.1 (**B**), 128.2 (**A**), 128.3 (**A**), 128.5 (**B**), 129.0 (**B**), 129.1 (**A**), 137,6 (**B**), 138.2 (**A**), 141.9 (**A**), 145.3 (**B**) ; MS *m/z* (rel intensity): 322 (M^+, 10), 237 (16), 217 (25), 133 (38), 105 (32), 91 (100). Anal. Calcd for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.65; H, 9.67.

(*E*)-1-(1-Phenyl-1-octenyl)cyclohexanol (A) and **(*E*)-1-(1-Hexyl-2-phenylethenyl)cyclohexanol (B).** The regioisomer ratio was determined by ^1H NMR analysis (**A**/**B**=79/21). Bp 147–149 °C (bath temp, 0.18 Torr); IR (neat, mixture of **A**/**B**=79/21): 3424, 2924, 2852, 1598, 1449, 1263, 738, 703cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.7–0.9 (m, 3H), 1.0–1.3 (m, 8H + 2H (**A**)), 1.3–1.8 (m, 11H),

2.1–2.3 (m, 2H (**B**)), 5.75 (t, *J*=7.3 Hz, 1H (**A**)), 6.59 (s, 1H (**B**)), 7.0–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.8, 22.8, 23.3, 26.3, 26.4, 29.0, 29.6, 29.7, 30.5, 30.6, 31.0, 32.2, 32.4, 37.4, 74.2 (**A**), 75.7 (**B**), 124.6 (**B**), 126.8 (**B**), 127.1 (**A**), 127.2 (**A**), 128.4 (**A**), 128.9 (**B**), 129.3 (**B**), 130,7 (**A**), 139.4 (**B**), 140.1 (**A**), 149.0 (**A**), 150.8 (**B**); MS *m/z* (rel intensity): 286 (M^+, 62), 268 (39), 201 (79), 117 (87), 91 (100). Anal. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56. Found: C, 83.89; H, 10.77.

(*E*)-2-Decyl-5-phenyl-l-(trimethylsilyl)-1-penten-3-ol (A) and **(Z)-1-Phenyl-4-(trimethylsilyl)-4-pentadecen-3-ol (B).** The regioisomer ratio was determined by ^{1}H NMR analysis (**A/B**=89/11). Bp 150–152 °C (bath temp, 0.18 Torr); IR (neat, mixture of **A/B**=89/11): 3336, 2922, 2852, 1612, 1456, 1248, 855, 837, 696 cm^{-}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9H (**A**)), 0.14 (s, 9H (**B**)), 0.7–1.0 (m, 3H), 1.1–1.5 (m, 17H), 1.7–2.4 (m, 4H), 2.6–2.9 (m, 2H), 4.0–4.2 (m, 1H (**A**)), 4.2–4.3 (m, 1H (**B**)), 5.52 (s, 1H (**A**)), 6.23 (t, *J*=7.6 Hz, 1H (**B**)), 7.1–7.4 (m, 5H); ^{13}C NMR (**A**, $CDCl_3$): δ 0.3, 14.2, 22.7, 29.3, 29.5, 29.6, 30.2, 30.5, 31.9, 32.2, 33.5, 38.0, 75.0, 122.2, 125.8, 128.3, 128.4, 142.1, 161.5; MS *m/z* (rel intensity): 374 (M^+, 1), 359 (4), 270 (13), 233 (16), 143 (57), 73 (100). Anal. Calcd for $C_{24}H_{42}OSi$: C, 76.94; H, 11.30. Found: C, 77.09; H, 11.47.

(*E*)-1-(1-Decyl-2-(trimethylsilyl)ethenyl)cyclohexanol. Bp 134–136 °C (bath temp, 0.20 Torr); IR (neat): 3410, 2924, 2852, 1600, 1459, 1247, 858 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.11 (s, 9H), 0.88 (t, *J*=6.5 Hz, 3H), 1.1–1.5 (m, 17H), 1.4–1.8 (m, 10H), 2.1–2.2 (m, 2H), 5.55 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 0.4, 14.1, 22.1, 22.7, 25.6, 29.3, 29.6, 29.7, 30.6, 31.9, 32.7, 32.8, 36.9, 75.5, 120.9, 166.0; MS *m/z* (rel intensity): 338 (M^+, 0.4), 323 (5), 320 (3), 122 (48), 73 (100). Anal. Calcd for $C_{21}H_{42}OSi$: C, 74.48 ; H, 12.50. Found: C, 74.32; H, 12.68.

(*E*)-2,5-Diphenyl-1-(trimethylsilyl)-1-penten-3-ol. $TaCl_5$ (4.0 equiv), zinc (6.0 equiv), and pyridine (8.0 equiv) were employed. Bp 144–146 °C (bath temp, 0.12 Torr); IR (neat): 3320, 2856, 1596, 1454, 1442, 1247, 1073, 860, 836,

699 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.19 (s, 9H), 1.6–2.0 (m, 2H), 1.6–1.8 (m, 1H), 2.60 (ddd, *J*=6.4, 10.1, 13.8 Hz, 1H), 2.75 (ddd, *J*=5.7, 10.1, 13.8 Hz, 1H), 4.3–4.4 (m, 1H), 5.86 (s, 1H), 7.1–7.4 (m, 10H); ^{13}C NMR ($CDCl_3$): δ −0.1, 31.8, 36.5, 76.8, 125.7, 126.4, 127.3, 127.8, 128.3, 128.4, 128.8, 140.9, 141.9, 160.5; MS *m/z* (rel intensity): 310 (M^+, 0.5), 295 (3), 277 (6), 206 (57), 91 (41), 73 (100). Anal. Calcd for $C_{20}H_{26}OSi$: C, 77.36; H, 8.44. Found: C, 77.44; H, 8.57.

(*E*)-1-(*tert*-Butyldimethylsilyl)-2-decyl-5-phenyl-1-penten-3-ol. $TaCl_5$ (4.0 equiv), zinc (6.0 equiv), and pyridine (8.0 equiv) were employed. Bp 157–159 °C (bath temp, 0.18 Torr); IR (neat): 3564, 2950, 2922, 2852, 1611, 1464, 1249, 836, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.08 (s, 3H), 0.09 (s, 3H), 0.8–1.0 (m, 3H), 0.88 (s, 9H), 1.1–1.5 (m, 16H), 1.45 (d, *J*=3.9 Hz, 1H), 1.7–2.1 (m, 2H), 2.1–2.3 (m, 2H), 2.5–2.9 (m, 2H), 4.1–4.2 (m, 1H), 5.55 (s, 1H), 7.1–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −4.1, −4.0, 14.1, 17.0, 22.7, 26.5, 29.3, 29.5, 29.6, 30.2, 30.5, 31.6, 31.9, 32.1, 33.8, 38.2, 75.2, 119.1, 125.8, 128.4, 128.5, 142.2, 162.3; MS *m/z* (rel intensity): 359 (M^+–*t*–Bu, 49), 135 (10), 91 (36), 75 (100), 57 (8). Anal. Calcd for $C_{27}H_{48}OSi$: C, 77.81; H, 11.61. Found: C, 77.70; H, 11.61.

(*E*)-1-(2-(*tert*-Butyldimethylsilyl)-1-decylethenyl)cyclohexanol. $TaCl_5$ (4.0 equiv), zinc (6.0 equiv), and pyridine (8.0 equiv) were employed. Bp 157–159 °C (bath temp, 0.22 Torr); IR (neat): 3462, 2924, 2852, 1601, 1465, 1252, 837 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.08 (s, 6H), 0.7–1.0 (m, 12H), 1.1–1.4 (m, 17H), 1.3–1.7 (m, 10H), 2.0–2.1 (m, 2H), 5.57 (s, 1H); ^{13}C NMR ($CDCl_3$): δ −4.1, 14.1, 17.1, 22.2, 22.7, 25.6, 26.6, 29.3, 29.6, 29.7, 30.5, 31.9, 32.8, 33.0, 37.2, 75.8, 117.9, 166.8; MS *m/z* (rel intensity): 323 (M^+–*t*–Bu, 45), 305 (47), 139 (17), 75 (100), 57 (14). Anal. Calcd for $C_{24}H_{48}OSi$: C, 75.71; H, 12.71. Found: C, 75.42; H, 12.71.

(*Z*)-5-Iodo-4-pentyl-1-phenyl-4-decen-3-ol (5). To a stirred solution of $TaCl_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and benzene (1:1, 10 mL) at 25 °C under an argon atmosphere was added zinc dust (0.20 g, 3.0 mmol), and the

mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in DME-benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C for 30 min. THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the reaction mixture was stirred at 25 °C for 15 min, 3-phenylpropanal (0.16 g, 1.2 mmol) was added to the mixture, and the resulting mixture was stirred at 25 °C for an additional 15 min. To the mixture was added at -25 °C a solution of I_2 (1.3 g, 5.0 mmol) in THF (6 mL) and the whole mixture was stirred at -25 °C for 10 min. Aqueous NaOH solution (15%, 2 mL) was added at -25 °C and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was filtered off with Hyflo-Super Cel and washed well with ethyl acetate (3x5 mL). The organic extracts were washed with saturated $NaHSO_3$ (10 mL) and brine. Organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the crude product by column chromatography on silica gel with ethyl acetate-hexane (1:20) gave 0.33 g (76 %) of (*Z*)-5-iodo-4-pentyl-1-phenyl-4-decen-3-ol. Bp 155-157 °C (bath temp, 0.18 Torr); IR (neat): 3342, 2952, 2926, 2856, 1654, 1618, 1466, 1050, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8-1.0 (m, 6H), 1.2-1.7 (m, 13H), 1.7-1.9 (m, 2H), 2.0-2.4 (m, 2H), 2.4-2.6 (m, 2H), 2.7-2.8 (m, 1H), 2.8-2.9 (m, 1H), 4.5-4.6 (m, 1H), 7.1-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.4, 22.6, 28.4, 29.5, 30.6, 30.8, 32.3, 32.4, 36.9, 41.2, 81.1, 106.5, 125.8, 128.3, 128.5, 141.8, 144.9; MS *m/z* (rel intensity): 410 (M^+-H_2O, 0.6), 301 (35), 196 (20), 105 (38), 91 (100). Anal. Calcd for $C_{21}H_{33}OI$: C, 58.88; H, 7.76. Found: C, 59.13; H, 7.94.

General Procedure for the Synthesis of Allylic Alcohols from Alkynes and α,β-Unsaturated Carbonyl Compounds. To a stirred solution of $TaCl_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and benzene (1:1, 10 mL) at 25 °C under an argon atmosphere was added zinc dust (0.20 g, 3.0 mmol) and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of an

alkyne (1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C. After consumption of the alkyne was confirmed by TLC, THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the reaction mixture was stirred at 0 °C for 15 min, α,β–unsaturated carbonyl compound (2.0 mmol) was added to the mixture at 0 °C, and the resulting mixture was stirred at 0°C for 30 min. Aqueous NaOH (15%, 2 mL) was added, and the mixture was stirred at 0 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo–Super Cel and washed well with ethyl acetate (3x5 mL). Organic extracts were concentrated *in vacuo* and diluted with hexane (10 mL), dried over $MgSO_4$, and concentrated again *in vacuo*. Purification of the crude product by column chromatography on silica gel gave the desired allylic alcohol.

(*E*)–4–Pentyl–1,4–decadien–3–ol (8). Bp 97–98 °C (bath temp, 0.18 Torr); IR (neat): 3334, 2926, 2856, 1726, 1648, 1466, 1378, 989, 919 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.2–1.6 (m, 12H), 1.49 (d, *J*=3.9 Hz, 1H), 1.9–2.2 (m, 4H), 4.5–4.6 (m, 1H), 5.14 (ddd, *J*=10.3, 1.5, 1.5 Hz, 1H), 5.28 (ddd, *J*=17.2, 1.5, 1.5 Hz, 1H), 5.47 (t, *J*=7.1 Hz, 1H), 5.86 (ddd, *J*=5.8, 10.3, 17.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.5, 22.6, 27.6, 27.7, 29.3, 29.4, 31.6, 32.2, 77.0, 114.6, 127.3, 139.9, 140.6; MS *m/z* (rel intensity): 224 (M^+, 4), 153 (64), 97 (31), 83 (100), 55 (87). Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.29; H, 12.82.

(*E*)–2–Methyl–4–pentyl–1,4–decadien–3–ol. Bp 105–107 °C (bath temp, 0.16 Torr); IR (neat): 3340, 2954, 2924, 2856, 1726, 1655, 1459, 897 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.2–1.5 (m, 12H), 1.55 (d, *J*=3.5 Hz, 1H), 1.62 (s, 3H), 1.9–2.2 (m, 4H), 4.4–4.5 (m, 1H), 4.92 (bs, 1H), 5.09 (bs, 1H), 5.49 (t, *J*=7.3 HZ, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 18.4, 22.4, 22.6, 27.4, 27.6, 29.2, 29.4, 31.6, 32.3, 79.6, 111.0, 127.7, 139.2, 145.8; MS *m/z* (rel intensity): 238 (M^+, 6), 167 (100), 97 (82), 71 (49), 55 (75). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68.

Found: C, 80.86; H, 12.96.

(*E*)-3-Methyl-4-pentyl-1,4-decadien-3-ol. Bp 92–94 °C (bath temp, 0.14 Torr); IR (neat): 3392, 2856, 2926, 1730, 1648, 1467, 1378, 1120, 918 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.2–1.5 (m, 12H), 1.38 (s, 3H), 1.42 (s, 1H), 1.9–2.1 (m, 4H), 5.06 (dd, *J*=10.6, 1.3 Hz, 1H), 5.23 (dd, *J*=17.3, 1.3 Hz, 1H), 5.50 (t, J=7.1 Hz, 1H), 5.92 (dd, J=10.6, 17.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.4, 22.5, 27.0, 27.9, 28.0, 29.5, 30.2, 31.6, 32.5, 76.1, 111.6, 125.4, 143.4, 144.6; MS *m/z* (rel intensity): 238 (M^+, 0.3), 220 (2), 167 (17), 71 (40), 43 (100). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.45; H, 12.76.

(*E*)-4-Hexyl-5-phenyl-1,4-pentadien-3-ol (A) and (*E*)-4-Phenyl-1,4-undecadien-3-ol (B). The regioisomer ratio was determined by ^1H NMR analysis (**A**/**B**=71/29). Bp 116–118 °C (bath temp, 0.18 Torr); IR (neat, mixture of **A**/**B**=71/29): 3340, 2952, 2922, 2854, 1728, 1459, 1072, 989, 920, 701 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 3H), 1.1–1.6 (m, 8H), 1.8–2.1 (m, 1H + 2H (**A**)), 2.1–2.4 (m, 2H (**B**)), 4.7–4.8 (m, 1H (**B**)), 4.8–4.9 (m, 1H (**A**)), 5.09 (dd, *J*=1.2, 10.3 Hz, 1H (**A**)), 5.18 (dd, *J*=1.1, 17.1 Hz, 1H (**A**)), 5.20 (d, *J*=10.3 Hz, 1H (**B**)), 5.35 (d, *J*=17.1 Hz, 1H (**B**)), 5.76 (t, *J*=7.4 Hz, 1H (**A**)), 5.87 (ddd, *J*=5.8, 10.3, 17.1 Hz, 1H (**A**)), 5.91 (ddd, *J*=5.8, 10.3, 17.1 Hz, 1H (**B**)), 6.59 (s, 1H (**B**)), 7.1–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.2, 22.8, 28.8, 29.1, 29.9, 31.7, 31.8, 77.5 (**A**), 77.9 (**B**), 115.3 (**A**), 115.7 (**B**), 126.0 (**B**), 126.7 (**B**), 127.1 (**A**), 128.1 (**A**), 128.3 (**B**), 128.8 (**B**), 129.0 (**A**), 129.7 (**A**), 137.8 (**B**), 138.4 (**A**), 139.5 (**A**), 139.7 (**B**), 142.2 (**A**), 144.0 (**B**); MS *m/z* (rel intensity): 244 (M^+, 7), 159 (74), 117 (80), 91 (100), 55 (50). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.61; H, 10.08.

(*E*)-3-Methyl-4-phenyl-1,4-undecadien-3-ol (A) and (*E*)-3-Methyl-4-hexyl-5-phenyl-1,4-pentadien-3-ol (B). The regioisomer ratio was determined by ^1H NMR analysis (**A**/**B**=71/29). Bp 112–114 °C (bath temp, 0.18 Torr); IR

(neat, mixture of **A**/**B**=71/29): 3392, 2952, 2924, 2854, 1721, 1466, 1116, 919, 703 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 3H), 1.1–1.6 (m, 8H), 1.35 (s, 3H (**A**)), 1.49 (s, 3H (**B**)), 1.7–1.8 (m, 1H + 2H (**A**)), 2.2–2.3 (m, 2H (**B**)), 5.07 (d, *J*=10.6 Hz, 1H (**A**)), 5.14 (d, *J*=10.5 Hz, 1H, (**B**)), 5.19 (d, *J*=17.1 Hz, 1H (**A**)), 5.32 (d, *J*=17.5 Hz, 1H (**B**)), 5.82 (t, *J*=7.2 Hz, 1H (**A**)), 6.01 (dd, *J*=10.6, 17.1 Hz, 1H (**A**)), 6.03 (dd, *J*=10.5, 17.5 Hz, 1H (**B**)), 6.67 (s, 1H (**B**)), 7.1–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.5, 27.3, 28.3, 28.8, 28.9, 29.6, 29.7, 29.8, 31.3, 31.6, 75.4 (**A**), 76.6 (**B**), 111.9 (**A**), 112.3 (**B**), 125.0 (**B**), 126.3 (**B**), 126.7 (**A**), 127.6 (**A**), 127.7 (**A**), 128.1 (**B**), 128.5 (**B**), 130.0 (**A**), 138.1 (**A**), 138.4 (**B**), 144.3 (**B**), 144.4 (**A**), 145.7 (**A**), 147.1 (**B**); MS *m/z* (rel intensity): 258 (M^+, 0.5), 240 (7), 200 (36), 117 (100), 91 (78), 43 (80). Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.96; H, 10.38.

(*E*)-4-Decyl-5-(trimethylsilyl)-1,4-pentadien-3-ol (A) and (*E*)-4-(Trimethylsilyl)-1,4-pentadecadien-3-ol (B). The regioisomer ratio was determined by ^1H NMR analysis (**A**/**B**=97/3). Bp 117–119 °C (bath temp, 0.20 Torr); IR (neat, mixture of **A**/**B**=97/3): 3338, 2922, 2852, 1728, 1617, 1466, 1247, 837 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.11 (s, 9H), 0.88 (t, *J*=6.0 Hz, 3H), 1.1–1.5 (m, 16H), 1.60 (d, *J*=4.3 Hz, 1H), 1.9–2.3 (m, 2H), 4.5–4.6 (m, 1H), 5.15 (ddd, *J*=10.2, 1.4, 1.4 Hz, 1H), 5.27 (ddd, *J*=17.1, 1.4, 1.4 Hz, 1H), 5.57 (s, 1H (**A**)), 5.80 (ddd, *J*=6.4, 10.2, 17.1 Hz, 1H), 6,24 (t, *J*=7.6 Hz, 1H (B)); ^{13}C NMR (**A**, $CDCl_3$): δ 0.2, 14.1, 22.6, 29.3, 29.5, 29.6, 29.8, 30.1, 31.9, 33.3, 76.7, 115.3, 122.8, 139.7, 159.3; MS *m/z* (rel intensity): 296 (M^+, 0.8), 281 (17), 165 (19), 80 (82), 73 (100). Anal. Calcd for $C_{18}H_{36}OSi$: C, 72.90; H, 12.24. Found: C, 73.14; H, 12.47.

(*E*)-4-Decyl-3-methyl-5-(trimethylsilyl)-1,4-pentadien-3-ol. Bp 114–116 °C (bath temp, 0.14 Torr); IR (neat): 3374, 2952, 2922, 2852, 1728, 1602, 1466, 1247, 857 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.10 (s, 9H), 0.87 (t, *J*=6.4 Hz, 3H), 1.2–1.5 (m, 16H), 1.40 (s, 3H), 1.53 (s, 1H), 2.1–2.2 (m, 2H), 5.06 (dd, *J*=1.2, 10.7

Hz, 1H), 5.22 (dd, *J*=1.2, 17.3 Hz, 1H), 5.58 (s, 1H), 5.94 (dd, J=10.7, 17.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 0.3, 14.1, 22.7, 27.6, 29.3, 29.5, 29.6, 30.4, 31.9, 32.2, 32.8, 77.3, 111.9, 122.6, 144.6, 162.6; MS *m/z* (rel intensity): 310 (M^+, 0.2), 295 (4), 165 (6), 73 (100), 43 (10). Anal. Calcd for $C_{19}H_{38}OSi$: C, 73.47; H, 12.33. Found: C, 73.27; H, 12.53.

(*E*)-1-(1-Cyclohexenyl)-2-decyl-3-(trimethylsilyl)-2-propen-1-ol (9). Bp 140–142 °C (bath temp, 0.18 Torr); IR (neat): 3346, 2924, 2852, 1730, 1617, 1459, 1247, 857, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.11 (s, 9H), 0.87 (t, *J*=6.5 Hz, 3H), 1.1–1.6 (m, 16H), 1.4–1.7 (m, 5H), 1.7–2.2 (m, 6H), 4.4–4.5 (m, 1H), 5.57 (s, 1H), 5.7–5.8 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 0.4, 14.1, 22.5, 22.6, 23.2, 25.2, 29.4, 29.5, 29.6, 30.1, 31.9, 33.4, 79.7, 122.0, 125.1, 138.1, 158.5; MS *m/z* (rel intensity): 350 (M^+, 1), 277 (3), 134 (8), 75 (22), 73 (100). Anal. Calcd for $C_{22}H_{42}OSi$: C, 75.35; H, 12.07. Found: C, 75.61; H, 12.20.

(1*E*,4*E*)-2-Decyl-1-(trimethylsilyl)-1,4-octadien-3-ol. Bp 131–133 °C (bath temp, 0.20 Torr); IR (neat): 3298, 2954, 2922, 2852, 1617, 1459, 1247, 967, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.11 (s, 9H), 0.87 (t, *J*=6.7 Hz, 3H), 0.89 (t, *J*=7.2 Hz, 3H), 1.1–1.5 (m, 18H), 1.56 (bs, 1H), 1.9–2.3 (m, 4H), 4.48 (d, *J*=7.2 Hz, 1H), 5.37 (dd, *J*=7.3, 15.6 Hz, 1H), 5.58 (s, 1H), 5.69 (dt, *J*=15.6, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 0.3, 13.7, 14.1, 22.3, 22.7, 29.3, 29.5, 29.6, 30.1, 31.9, 33.5, 34.3, 121.7, 131,7, 133.0, 160.0; MS *m/z* (rel intensity): 338 (M^+, 0.3), 323 (1), 265 (1), 75 (19), 73 (100). Anal. Calcd for $C_{21}H_{42}OSi$: C, 74.48; H, 12.50. Found: C, 74.58; H, 12.39.

(*E*)-2-Decyl-1-(*tert*-butyldimethylsilyl)-1,4-pentadien-3-ol. Bp 135–137 °C (bath temp, 0.18 Torr); IR (neat): 3338, 2950, 2924, 2852, 1729, 1617, 1465, 1248, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.08 (s, 3H), 0.09 (s, 3H), 0.8–0.9 (m, 3H), 0.87 (s, 9H), 1.2–1.5 (m, 16H), 1.59 (d, *J*=4.3 Hz, 1H), 2.0–2.3 (m, 2H), 4.5–4.6 (m, 1H), 5.14 (ddd, *J*=1.4, 1.4, 10.2 Hz, 1H), 5.27 (ddd, *J*=1.4, 1.4, 17.1 Hz,

1H), 5.59 (s, 1H), 5.80 (ddd, *J*=6.4, 10.2, 17.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ −4.2, −4.1, 14.1, 17.0, 22.7, 26.6, 29.3, 29.5, 29.6, 30.1, 30.2, 31.9, 33.6, 77.0, 115.4, 119.8, 139.9, 160.3; MS *m/z* (rel intensity): 338 (M^+, 0.1), 281 (92), 115 (9), 75 (100), 73 (75). Anal. Calcd for $C_{21}H_{42}OSi$: C, 74.48; H, 12.50. Found: C, 74.33; H, 12.80.

(*E*)−1−(1−Cyclohexyl)−2−decyl−3−(trimethylsilyl)−2−propen−1−one (10).[15] To a stirred suspension of NiO_2 (12 g, f=0.15, 1.8 mmol) in benzene (10 mL) was added at 0 °C a solution of the allylic alcohol **9** (0.35 g, 1.0 mmol) in benzene (5 mL). The resulting mixture was stirred at 50 °C for 2 h. NiO_2 was removed by filtration and washed with benzene (3x5 mL). Organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel with ethyl acetate−hexane (1:40) as eluent gave 0.30 g (85%) of (*E*)−1−(1−cyclohexyl)−2−decyl−3−(trimethylsilyl)−2−propen−1−one (**10**) as a colorless liquid: Bp 129−131 °C (bath temp, 0.18 Torr); IR (neat): 2924, 2852, 1644, 1451, 1249, 1220, 856, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.15 (s, 9H), 0.85 (t, *J*=6.5 Hz, 3H), 1.1−1.4 (m, 16H), 1.5−1.7 (m, 4H), 2.1−2.3 (m, 4H), 2.3−2.5 (m, 2H), 5.76 (s, 1H), 6.62 (bs, 1H); ^{13}C NMR ($CDCl_3$): δ 0.0, 14.1, 21.7, 22.0, 22.7, 23.6, 26.1, 29.1, 29.3, 29.4, 29.5, 29.8, 31.9, 33.1, 134.7, 138.6, 142.3, 156.8; MS *m/z* (rel intensity): 348 (M^+, 4), 333 (14), 275 (4), 221 (25), 73 (100). Anal. Calcd for $C_{22}H_{40}OSi$: C, 75.79; H, 11.56. Found: C, 75.53; H, 11.78.

8−Decylbicyclo[4.3.0]−8−nonen−7−one (11): To a stirred solution of the divinyl ketone **10** (0.34 g, 1.0 mmol) in CH_2Cl_2 (10 mL) at −25 °C under an argon atmosphere was added $FeCl_3$ (0.18 g, 1.1 mmol). After being stirred at −25 °C for 40 min, the reaction mixture was poured into water and extracted with ether. The organic extracts were washed with brine and dried over $MgSO_4$. Purification of the crude product by column chromatography on silica gel with ethyl acetate−hexane (1:20) as eluent gave 0.23 g (82%) of 8−decylbicyclo[4.3.0]−8−nonen−7−one (**11**)

as a colorless liquid. Bp 132–134 °C (bath temp, 0.18 Torr); IR (neat): 2922, 2852, 1706, 1459 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.8Hz, 3H), 1.0–1.6 (m, 14H), 1.5–1.7 (m, 6H), 1.7–2.1 (m, 4H), 2.17 (t, *J*=7.5 Hz, 2H), 2.42 (dt, *J*=6.3, 6.4 Hz, 1H), 2.8–3.0 (m, 1H), 7.21 (bs, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 21.1, 21.2, 22.6, 22.8, 24.8, 27.7, 28.2, 29.3, 29.5, 31.9, 38.6, 45.8, 144.4, 160.2, 211.6; MS *m/z* (rel intensity): 276 (M^+, 50), 191 (28), 151 (100), 81 (27), 43 (35). Anal. Calcd for $C_{19}H_{32}O$: C, 82.55; H, 11.67. Found: C, 82.28; H, 11.80.

Typical Procedure for Reactions between a Tantalum–6–dodecyne Complex and α,β–Unsaturated Compounds Having a β–Substituent. To a stirred solution of $TaCl_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and benzene (1:1, 10 mL) at 25 °C under an argon atmosphere was added zinc dust (0.20 g, 3.0 mmol), and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 6–dodecyne (0.16 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C for 30 min. THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the reaction mixture was stirred at 0 °C for 15 min, 2–hexenal (0.20 g, 2.0 mmol) was added to the mixture, and the resulting mixture was stirred at 0°C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 0 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo–Super Cel and washed well with ethyl acetate (3x5 mL). Organic extracts were concentrated *in vacuo*, diluted with hexane, dried over $MgSO_4$, and concentrated again *in vacuo*. Purification of the crude product by column chromatography on silica gel (ethyl acetate–hexane, 1:30–1:5) gave 52 mg (15 %) of 2,5–dihydrofuran **13** and 0.13 g (49 %) of (4*E*,7*E*)–7–pentyl–4,7–tridecadien–6–ol (**12**).

(*E*,*E*)–2,5–Di–(1–Pentenyl)–3,4–dipentyl–3–oxolene (13). Two isomers were produced, and the ratio was determined by ^1H NMR analysis

(major/minor=92/8). Bp 137–139 °C (bath temp, 0.18 Torr); IR (neat, mixture of major/minor=92/8): 2954, 2926, 2858, 1719, 1664, 1466, 966 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 12H), 1.1–1.5 (m, 16H), 1.8–2.3 (m, 8H), 4.95 (d, *J*=8.1 Hz, 2H(minor)), 5.04 (d, *J*=7.6 Hz, 2H(major)) 5.2–5.4 (m, 2H), 5.68 (dt, *J*=7.6, 8.4 Hz, 2H); ^{13}C NMR (major, $CDCl_3$): δ 13.6, 14.0, 22.3, 22.4, 25.0, 27.5, 31.7, 34.2, 88.3, 130.6, 133.9, 134.4; MS *m/z* (rel intensity): 346 (M^+, 18), 302 (36), 275 (100), 249 (77), 97 (55). Anal. Calcd for $C_{24}H_{42}O$: C, 83.17; H, 12.21. Found: C, 82.97; H, 12.42.

(4*E*,7*E*)-7-Pentyl-4,7-tridecadien-6-ol (12). Bp 120–122 °C (bath temp, 0.20 Torr); IR (neat): 3316, 2954, 2924, 2856, 1648, 1466, 1378, 966 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 9H), 1.2–1.5 (m, 15H), 1.9–2.2 (m, 6H), 4.4–4.5 (m, 1H), 5.44 (dd, *J*=6.7, 15.2 Hz, 1H), 5.47 (t, *J*=6.7 Hz, 1H), 5.68 (dt, *J*=15.2, 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 13.7, 14.0, 22.3, 22.5, 22.6, 27.6, 27.8, 29.3, 29.5, 31.6, 32.2, 34.3, 76.7, 126.3, 131.8, 140.1; MS *m/z* (rel intensity): 266 (M^+, 6), 223 (14), 195 (49), 99 (25), 71 (81), 43 (100). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; 12.86. Found: C, 81.16; H, 12.97.

Reactions between Oxatantallacyclopentene, Derived from a Tantalum-6-dodecyne Complex and 3-Phenylpropanal, and α,β-Unsaturated Carbonyl Compounds. A tantalum-6-dodecyne complex prepared as described above from 6-dodecyne (0.17 g, 1.0 mmol), $TaCl_5$ (0.72 g, 2.0 mmol) and zinc dust (0.20 g, 3.0 mmol) in DME and benzene (1:1, 10 mL) was treated with THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) at 25 °C for 15 min. To the reaction mixture was added 3-phenylpropanal (0.16 g, 1.2 mmol), and the mixture was stirred at 25 °C for 15 min. α,β-Unsaturated carbonyl compound (2.0 mmol) was added, and the resulting mixture was stirred at 25°C for 3 h. Aqueous NaOH solution (15%, 2 mL) was added to the mixture and stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-

Super Cel and washed well with ethyl acetate (3x5 mL). Organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel.

4,5-Dipentyl-1-phenyl-5,7-octadien-3,4-diol. Major isomer: R_f=0.55 (ethyl acetate-hexane, 1:3); bp 154-156 °C (bath temp, 0.18 Torr); IR (neat): 3402, 2952, 2928, 2858, 1456, 1052, 786, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.86 (t, *J*=6.5 Hz, 3H), 0.89 (t, *J*=6.5 Hz, 3H), 0.9-1.6 (m, 12H), 1.5-1.8 (m, 3H), 1.8-2.3 (m, 5H), 2.5-2.8 (m, 1H), 2.8-3.0 (m, 1H), 3.4-3.6 (m, 1H), 5.12 (dd, *J*=10.5, 17.5 Hz, 2H), 6.05 (d, *J*=11.0 Hz, 1H), 6.53 (ddd, *J*=10.5, 11.0, 17.5 Hz, 1H), 7.1-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.3, 22.6, 22.9, 28.5, 29.8, 32.2, 32.4, 32.5, 33.1, 36.8, 75.4, 80.6, 116.9, 125.7, 126.0, 128.3, 128.5, 132.8, 142.0, 143.8; MS *m/z* (rel intensity): 358 (M^+, 1), 340 (1), 223 (100), 105 (16), 91 (60), 71 (17). Anal. Calcd for $C_{24}H_{38}O_2$: C, 80.39; H, 10.68. Found: C, 80.11; H, 10.78. Minor isomer: R_f=0.61 (ethyl acetate-hexane, 1:3); bp 154-156 °C (bath temp, 0.18 Torr); IR (neat): 3432, 2952, 2926, 2858, 1457, 1051, 787, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.85 (t, *J*=6.5 Hz, 3H), 0.90 (t, *J*=6.5 Hz, 3H), 0.9-1.8 (m, 14H), 1.8-2.0 (m, 4H), 2.0-2.3 (m, 2H), 2.5-2.8 (m, 1H), 2.8-3.1 (m, 1H), 3.5-3.7 (m, 1H), 5.17 (dd, *J*=10.6, 17.1 Hz, 2H), 6.15 (d, *J*=11.0 Hz, 1H), 6.56 (ddd J=10.6, 11.0, 17.1 Hz, 1H), 7.1-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.4, 22.6, 23.2, 28.3, 30.5, 31.6, 32.3, 32.6, 34.5, 73.7, 80.6, 117.6, 125.8, 127.2, 128.4, 128.5, 132.7, 142.2, 144.8; MS *m/z* (rel intensity): 340 (M^+-H_2O, 3), 223 (84), 151 (44), 105 (36), 91 (100), 71 (24). Anal. Calcd for $C_{24}H_{38}O_2$: C, 80.39; H, 10.68. Found: C, 80.15; H, 10.82.

(*Z*)-4,5-Dipentyl-8-phenyl-1,4-octadien-3,6-diol. The isomer ratio was determined by ^1H NMR analysis (major/minor=89/11). R_f=0.46 (ethyl acetate-hexane, 1:3); bp 152-154 °C (bath temp, 0.16 Torr); IR (neat, mixture of major/minor=89/11): 3312, 2954, 2924, 2858, 1454, 786, 697 cm^{-1}; ^1H NMR

($CDCl_3$): δ 0.89 (t, *J*=6.7 Hz, 6H), 1.2–1.6 (m, 14H), 1.6–2.1 (m, 2H), 1.8–2.3 (m, 4H), 2.5–2.7 (m, 1H), 2.7–2.9 (m, 1H), 4.4–4.5 (m, 1H (minor)), 4.5–4.6 (m, 1H (major)), 4.9–5.0 (m, 1H), 5.07 (ddd, *J*=10.4, 1.5, 1.5 Hz, 1H), 5.19 (ddd, *J*=17.2, 1.5, 1.5 Hz, 1H), 5.91 (ddd, *J*=5.1, 10.4, 17.2 Hz, 1H), 7.1–7.4 (m, 5H); ^{13}C NMR (major, $CDCl_3$): δ 14.1, 22.5, 29.5, 29.7, 30.2, 30.5, 32.4, 32.6, 32.7, 32.8, 37.4, 71.4, 73.1, 114.1, 125.8, 128.4, 128.5, 137.6, 140.0, 141.9; MS *m/z* (rel intensity): 340 (M^+-H_2O, 10), 235 (97), 133 (21), 105 (71), and 91 (100). Anal. Calcd for $C_{24}H_{38}O_2$: C, 80.39; H, 10.68%. Found: C, 80.46; H, 10.95.

2-(1-Pentenyl)-3,4-dipentyl-5-(2-phenylethyl)-3-oxolene. The isomer ratio was determined by ^1H NMR analysis (major/minor=70/30). R_f=0.84 (ethyl acetate–hexane, 1:5); bp 148–150 °C (bath temp, 0.18 Torr); IR (neat, mixture of major/minor=70/30): 2954, 2926, 2856, 1728, 1456, 1071, 966, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 9H), 1.1–1.6 (m, 14H), 1.8–2.3 (m, 8H), 2.6–2.8 (m, 2H), 4.8–4.9 (m, 1H (minor)), 4.9–5.0 (m, 1H (major)), 5.0–5.2 (m, 1H), 5.33 (dd, *J*=8.2, 15.1 Hz, 1H), 5.72 (dt, *J*=15.1, 7.2 Hz, 1H), 7.1–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 13.7, 14.0, 22.3, 22.5, 24.9, 25.1, 25.2, 25.3, 27.5, 27.7, 31.1, 31.3, 31.7, 31.8, 31.9, 34.3, 36.5, 36.9, 85.6, 88.4, 88.5, 125.6, 128.3, 128.4, 128.5, 130.8, 131.4, 133.6, 133.8, 134.2, 134.3, 134.6, 142.7, 142.8; MS *m/z* (rel intensity): 382 (M^+, 22), 311 (64), 277 (89), 237 (68), 91 (100), 55 (51). Anal. Calcd for $C_{27}H_{42}O$: C, 84.75; H, 11.06. Found: C, 84.51; H, 11.26.

4,5-Dipentyl-1-phenyl-5,7-undecadien-3,4-diol. Major isomer: R_f=0.40 (ethyl acetate–hexane, 1:5); bp 162–164 °C (bath temp, 0.18 Torr); IR (neat): 3404, 2954, 2928, 2860, 1457, 967, 786, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 9H), 1.0–1.8 (m, 16H), 1.7–2.0 (m, 3H), 2.0–2.2 (m, 5H), 2.5–2.7 (m, 1H), 2.8–3.0 (m, 1H), 3.4–3.6 (m, 1H), 5.67 (dt, *J*=14.6, 7.0 Hz, 1H), 5.99 (d, *J*=11.0 Hz, 1H), 6.18 (dd, *J*=11.0, 14.6 Hz, 1H), 7.1–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 13.8, 14.1, 22.3, 22.6, 22.9, 28.4, 29.7, 32.2, 32.5, 33.2, 35.1, 36.7, 75.5, 80.7,

125.4, 125.7, 126.2, 128.3, 128.6, 135.5, 141.6, 143.0; MS *m/z* (rel intensity): 353 ($M^+-H_2O-C_2H_5$, 3) 265 (100), 221 (18), 91 (61), 43 (38). Anal. Calcd for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 81.03; H, 10.98. Minor isomer: R_f=0.55 (ethyl acetate–hexane, 1:5); bp 162–164 °C (bath temp, 0.18 Torr); IR (neat): 3434, 2952, 2928, 2866, 1457, 968, 786, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.7–1.1 (m, 9H), 1.0–1.5 (m, 14H), 1.6–2.0 (m, 5H), 2.0–2.3 (m, 5H), 2.6–2.8 (m, 1H), 2.8–3.0 (m, 1H), 3.5–3.6 (m, 1H), 5.71 (dt, *J*=14.0, 6.9 Hz, 1H), 6.11 (d, *J*=10.9 Hz, 1H), 6.23 (dd, *J*=10.9, 14.0 Hz, 1H), 7.1–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 13.8, 14.1, 22.4, 22.5, 23.2, 28.2, 30.3, 31.5, 32.3, 32.6, 34,4, 35.1, 73.6, 80.6, 125.7, 126.2, 126.8, 128.3, 128.5, 135.3, 141.2, 142.3; MS *m/z* (rel intensity): 353 ($M^+-H_2O-C_2H_5$, 8), 265 (53), 221 (40), 91 (100), 43 (56). Anal. Calcd for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 81.04; H, 10.87.

7–Methyl–4,5–dipentyl–1–phenyl–5,7–octadiene–3,4–diol. Major isomer: R_f=0.38 (ethyl acetate–hexane, 1:5); bp 154–156 °C (bath temp, 0.18 Torr); IR (neat): 3362, 2952, 2928, 2858, 1726, 1458, 1274, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.0–1.5 (m, 12H), 1.4–2.0 (m, 6H), 1.75 (s, 3H), 1.8–2.1 (m, 2H), 2.5–2.7 (m, 1H), 2.8–3.0 (m, 1H), 3.4–3.5 (m, 1H), 4.79 (bs, 1H), 4.93 (bs, 1H), 5.82 (s, 1H), 7.1–7.3 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.3, 22.6, 22.9, 23.8, 28.8, 29.8, 32.2, 32.5, 33.0, 37.1, 75.7, 80.7, 113.7, 125.8, 127.8, 128.3, 128.5, 142.0, 142.3; MS *m/z* (rel intensity): 323 ($M^+-C_6H_5$, 2), 237 (100), 181 (12), 91 (39), 43 (33). Anal. Calcd for $C_{25}H_{40}O_2$: C, 80.59; H, 10.82. Found: C, 80.47; H, 10.83. Minor isomer: R_f=0.51 (ethyl acetate–hexane, 1:5); bp 154–156 °C (bath temp, 0.18 Torr); IR (neat): 3454, 2954, 2928, 2860, 1726, 1457, 1272, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.0–1.6 (m, 12H), 1.6–2.0 (m, 6H), 1.86 (s, 3H), 2.1–2.3 (m, 2H), 2.6–2.8 (m, 1H), 2.8–3.0 (m, 1H), 3.5–3.7 (m, 1H), 4.85 (bs, 1H), 4.97 (bs, 1H), 5.99 (s, 1H), 7.1–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.3, 22.5, 23.2, 23.8, 28.4, 30.4, 31.5, 32.2, 32.5, 32.6, 34.7, 73.8, 80.7, 114.1, 125.8,

128.3, 128.5, 129.4, 140.2, 142.2, 143.2; MS *m/z* (rel intensity): 372 (M^+, 0.4), 323 (3), 237 (100), 91 (45), 71(14). Anal. Calcd for $C_{25}H_{40}O_2$: C, 80.59; H, 10.82. Found: C, 80.35; H, 11.07.

(*Z*)-2-Methyl-4,5-dipentyl-8-phenyl-1,4-octadien-3,6-diol. Major isomer: R_f=0.24 (ethyl acetate-hexane, 1:5); bp 158-160 °C (bath temp, 0.18 Torr); IR (neat): 3264, 2954, 2926, 2858, 1728, 1455, 1058, 1038, 786, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8-1.0 (m, 6H), 1.2-1.6 (m, 12H), 1.65 (s, 3H), 1.8-2.2 (m, 7H), 2.23 (d, *J*=3.8 Hz, 1H), 2.5-2.9 (m, 2H), 4.5-4.7 (m, 1H), 4.79 (bs, 1H), 4.86 (d, *J*=1.5 Hz, 1H), 5.02 (d, *J*=1.5 Hz, 1H), 7.1-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 20.3, 22.4, 29.7, 29.8, 30.1, 30.3, 32.6, 32.7, 37.6, 71.4, 74.3, 109.8, 125.7, 128.3, 128.4, 136.8, 140.9, 141.9, 146,7; MS *m/z* (rel intensity): 354 (M^+-H_2O, 13), 283 (41), 249 (86), 105 (41), 91 (100). Anal. Calcd for $C_{25}H_{40}O_2$: C, 80.59; H, 10.82. Found: C, 80.45; H, 11.03. Minor isomer: R_f=0.15 (ethyl acetate-hexane, 1:5); bp 160-162 °C (bath temp, 0.20 Torr); IR (neat): 3350, 2952, 2626, 2860, 1655, 1455, 1041, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8-1.0 (m, 6H), 1.1-1.7 (m, 12H), 1.57 (s, 3H), 1.67 (s, 1H), 1.7-1.8 (m, 1H), 1.9-2.2 (m, 6H), 2.6-2.8 (m, 1H), 2.8-3.0 (m, 1H), 4.7-4.8 (m, 1H), 4.91 (bs, 2H), 5.04 (bs, 1H), 7.2-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 20.2, 22.3, 22.4, 28.2, 28.5, 30.3, 30.6, 32.5, 32.6, 32.7, 32.8, 37.0, 69.8, 72.9, 109.7, 125.8, 128.4, 136.7, 141.4, 141.9, 146,0; MS *m/z* (rel intensity): 354 (M^+-H_2O, 6.6), 283 (36), 249 (28), 105 (36), 91 (100). Anal. Calcd for $C_{25}H_{40}O_2$: C, 80.59; H, 10.82. Found: C, 80.57; H, 11.04.

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CHAPTER 4

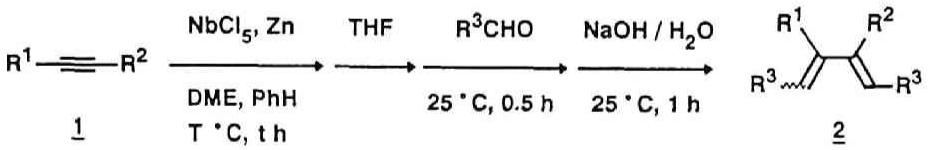
One-to-Two Addition Reaction of Niobium-Alkyne Complexes to Aldehydes and Sequential Deoxygenation Leading to 1,3-Dienes.

Niobium-alkyne complexes *in situ*, derived by treatment of alkynes with $NbCl_5$ and zinc, add to aldehydes in a one-to-two fashion to give 1,3-diene derivatives. The compounds are produced through (i) addition of the alkyne complexes with two equiv of aldehyde groups at *cis* vicinal positions of the alkenes and (ii) deoxygenative elimination of 2,7-dioxanioba-4-cycloheptene complexes.

A number of metal–alkyne complexes have been isolated in the last decade and their reactivities toward unsaturated compounds have been examined.[1-5] Insertion of carbonyl groups into metal–carbon bonds of such alkyne complexes of zirconium,[1] niobium,[2] and tantalum,[3] takes place, and oxametalacyclopentene complexes[6] are produced. Thus, one terminus of the metal–alkyne complex is employed as an alkene anion equivalent. Although the other metal–carbon bond of the complex still exists, it has not been employed as a nucleophilic center until recently. Pedersen[2a] and we[2b] have reported independently that niobium–alkyne complexes are produced by treating alkynes with low-valent niobium such as $NbCl_3$(DME) and $NbCl_5$–Zn and that reaction of the niobium–alkyne complexes with phthalaldehyde, which has two formyl groups at the suitable positions for cyclization, gave 1–naphthols.[2a,2b] We have found that the reactivity of niobium–alkyne complexes, prepared by $NbCl_5$–Zn, toward simple aldehydes is different from that of the complexes prepared from $NbCl_3$(DME) and that the former niobium–alkyne complexes add to two equiv of aldehydes at the *cis* vicinal alkene carbons to give 1,3–diene derivatives (Scheme 1).

When niobium–1–dodecyne complex,[7,8] derived from 1–dodecyne and a $NbCl_5$–Zn system, was treated with excess 3–phenylpropanal at 25 °C, 1,3–diene **2a** was produced after 30 min of stirring (Table 1, run 2). New carbon–carbon bonds were formed at vicinal positions of the alkyne. Other results are shown in Table 1. While trisubstituted ethene moieties were produced as mixtures of *E* and *Z*, disubstituted ones had *E* configuration (runs 1–3). In the case of an internal alkyne, dehydration products **3b** and **4b**, derived from one–to–one adduct, were produced as byproducts (run 4). Treatment of a niobium–1–dodecyne complex with cyclohexanone in DME–benzene–THF (1:1:1) gave the analogous dehydration product **5** in 60% yield (run 5).

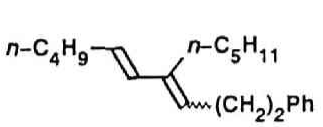
Table 1. Preparation of Substituted 1,3-Butadienes from Alkynes and Aldehydes.[a]



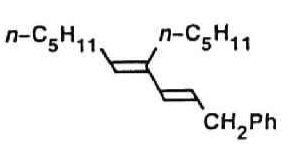
1 2

Run	R^1	R^2	R^3	T / °C	t / h	Yield / %[b]	*E* / *Z*[c]
1	*n*-$C_{10}H_{21}$	H	Ph	0	1	41	75 / 25
2			$Ph(CH_2)_2$	0	1	74 (**2a**)	63 / 37
3	Ph	H	*n*-C_8H_{17}	0	1	58	43 / 57
4	*n*-C_5H_{11}	*n*-C_5H_{11}	$Ph(CH_2)_2$	25	8	59[d] (**2b**)	68 / 32[e]
5	*n*-$C_{10}H_{21}$	H	(cyclohexanone)	0	1	0[f]	–

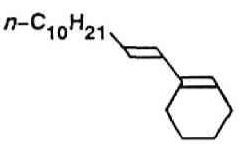
a) See, Experimental Section. b) Isolated yields. c) The isomer ratios were determined by ^1H NMR analysis. d) 1,3-Dienes (**3** and **4**) were obtained in 26% combined yields. e) The *E*/*Z* ratio indicates (3*E*,5*E*)/(3*E*,5*Z*). f) 1,3-Diene **5** was produced in 60% yield.



3b



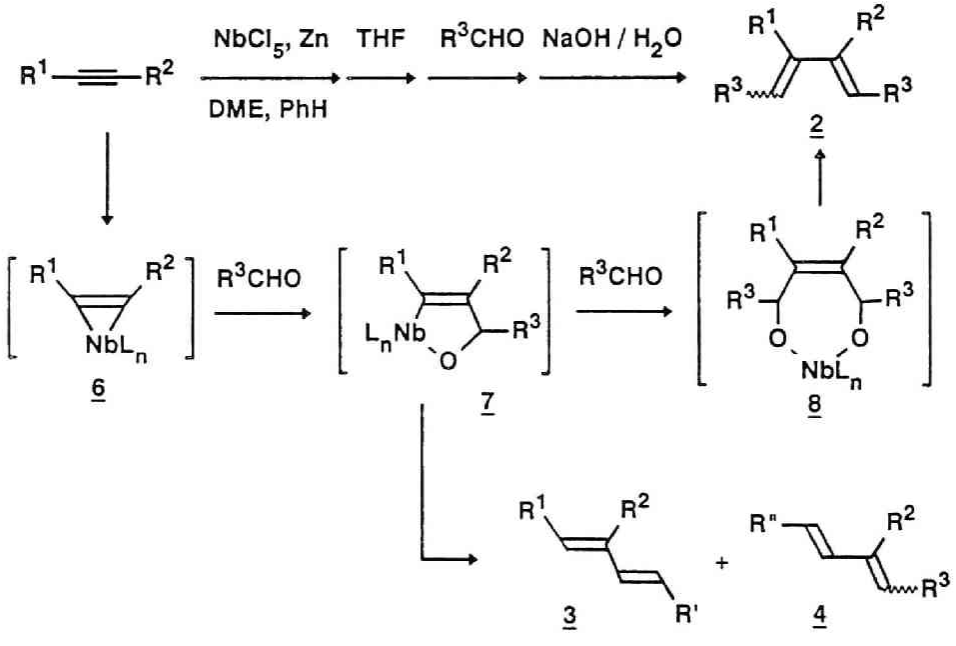
4b



5

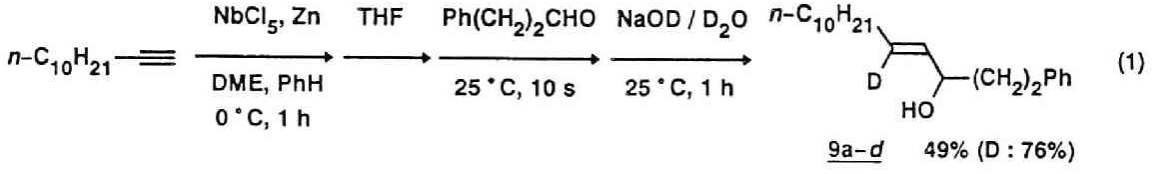
Formation of 1,3-dienes could be explained by the following mechanism shown in Scheme 1. (1) Treatment of alkynes with the low-valent niobium forms a niobium-alkyne complex **6**. (2) Addition of niobium-alkyne complex **6** to an aldehyde affords **7**, which adds smoothly to another aldehyde to give a niobium salt of 2-butene-1,4-diol **8**. (3) Deoxygenative elimination of two oxygen groups from niobium salt **8** gives 1,3-diene **2**.

Scheme 1



Allylic alcohol **9a**, hydrolyzed product of the one-to-one adduct **7a** (**a**: R^1=*n*-$C_{10}H_{21}$, R^2=H, R^3=Ph$(CH_2)_2$), was observed by TLC at the early stage of the reaction. The opposite regioisomer, 2-decyl-5-phenyl-1-penten-3-ol, was not obtained as in the case of tantalum-alkyne complexes.[3b] As reaction time went by, 1,3-diene **2a** increased gradually with decreasing allylic alcohol **9a**. When a NaOD/D_2O solution (15%) was added to the reaction mixture after 10 sec of the addition of 3-phenylpropanal, deuterated allylic alcohol **9a-*d*** was obtained in 49%

yield (content of deuterium: 76%) (eq 1). Hydrolyzed product of the niobium–diol complex **8a** (**a**: R^1=*n*–$C_{10}H_{21}$, R^2=H, R^3=Ph$(CH_2)_{2)}$) was not observed throughout the reaction. These results suggest that the second insertion process **7 -> 8** is almost as fast as the first insertion **6 -> 7** and that sequential deoxygenation **8 -> 2** proceeds very fast. It is reported that deoxygenative elimination of 2–butene–1,4–diols to 1,3–butadienes using low–valent titanium requires heating at reflux (THF solution) to complete the reaction.[7] Thus, strong oxophilicity of niobium facilitates the deoxygenative elimination under milder conditions.

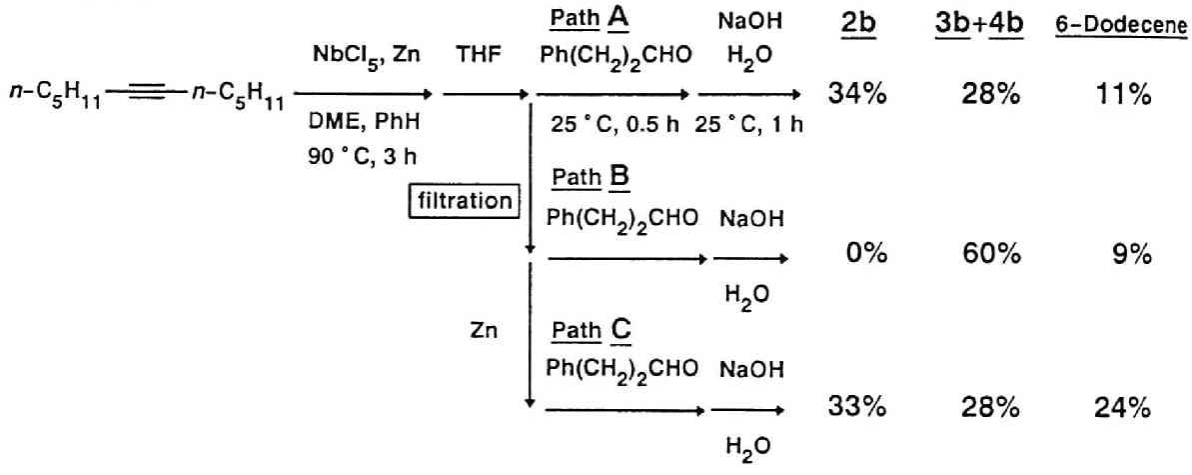


(1)

Considerable difference between the $NbCl_5$–Zn system[2b,8] and $NbCl_3$(DME)[2a] was observed. In contrast to the $NbCl_5$–Zn system, treatment of the niobium–6–dodecyne complex derived from the alkyne and $NbCl_3$(DME) with 3–phenylpropanal did not afford 1,3–diene **2b**.[10] To examine the effect of the excess amounts of zinc in the $NbCl_5$–Zn system, the experiments in Scheme 2 were conducted. Although the reaction with 4 mol of niobium per mol of alkyne gave the best results, the amounts of the niobium could be reduced to 1.2 mol in the case of internal alkynes.[11] Treatment of the reaction mixture of a niobium–6–dodecyne complex, derived from 1.0 equiv of 6–dodecyne, 1.2 equiv of $NbCl_5$, and 1.8 equiv of zinc in DME–benzene–THF (1:1:1), with 3–phenylpropanal at 25 °C gave 1,3–diene **2b** in 34% yield after alkaline workup along with dehydrated one–to–one products **3b** and **4b** in 28% combined yields and 6–dodecene in 11% yield (path A). The same reaction mixture of a niobium–6–dodecyne complex was filtered, and the filtrate was divided into two parts. Zinc dust (1.8 mol) was added to one of

the filtrates (path C), and then 3-phenylpropanal was introduced into both mixtures. The desired 1,3-diene **2b** was not detected without zinc, and a mixture of **3b** and **4b** was obtained in 60% yield (path B), while **2b** was produced in 33% yield (*E*/*Z* = 88/12) in the presence of additional zinc (path C). These results suggest that the presence of zinc in the reaction mixture is indispensable for the second insertion of aldehydes into the niobium complex **7** (Scheme 1, **7** -> **8**). Reduction of niobium complex **8** with zinc takes place also for promoting deoxygenation (**8** -> **2**).[9]

Scheme 2



Experimental Section

General Procedure for the Synthesis of 1,3-Diene Derivatives. In a 50-mL reaction flask was placed $NbCl_5$ (1.1 g, 4.0 mmol) under an argon atmosphere. To the salt was added at 25 °C benzene (5 mL) and DME (5 mL) successively. Zinc dust (0.39 g, 6.0 mmol) was added to a stirring pale orange solution of $NbCl_5$, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned to dark brown with slightly exothermic process. To the mixture was added at 0 °C a solution of an alkyne (1.0 mmol) in DME-benzene (1:1, 2 mL), and the whole mixture was stirred at 0 °C. After the consumption of the alkyne was confirmed by TLC, THF (6 mL) was added at 25 °C to the mixture and the resulting mixture was stirred for an additional 15 min. A carbonyl compound (4.0 mmol) was added to the mixture at 25 °C, and the mixture was stirred at 25 °C for another 30 min. Aqueous NaOH solution (15%, 4 mL) was added, and the mixture was stirred at 25 °C for 1 h. The deposited brown solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the crude product by column chromatography on silica gel with hexane as an eluent gave 1,3-diene derivatives.

(1*E*,3*E*)-2-Decyl-1,4-diphenyl-1,3-butadiene. R_f=0.53 (hexane); bp 180-182 °C (bath temp, 0.24 Torr); IR (neat): 2922, 2850, 1729, 1492, 1466, 1445, 958, 743, 690 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.89 (t, *J*=6.3 Hz, 3H), 1.2-1.6 (m, 14H), 1.5-1.8 (m, 2H), 2.5-2.6 (m, 2H), 6.62 (s, 1H), 6.66 (d, *J*=15.7 Hz, 1H), 6.89 (d, *J*=15.7 Hz, 1H), 7.2-7.6 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 27.8, 29.2, 29.4, 29.6, 30.0, 31.9, 126.4, 126.5, 126.7, 127.3, 127.6, 128.3, 128.6, 128.8, 131.8, 133.3, 137.7, 140.9; MS *m/z* (rel intensity): 346 (M^+, 18), 205 (100), 129 (22), 91 (24), 43 (8). Anal. Calcd for $C_{26}H_{34}$: C, 90.11; H, 9.89. Found: C, 90.37; H,

10.11.

(1*Z*,3*E*)-2-Decyl-1,4-diphenyl-1,3-butadiene. R_f=0.60 (hexane); bp 180-182 °C (bath temp, 0.24 Torr); IR (neat): 2922, 2852, 1730, 1492, 1465, 1448, 749, 695 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.6 Hz, 3H), 1.2-1.6 (m, 14H), 1.5-1.8 (m, 2H), 2.4-2.6 (m, 2H), 6.54 (s, 1H), 6.65 (d, *J*=16.5 Hz, 1H), 6.73 (d, *J*=16.5 Hz, 1H), 7.2-7.5 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 29.1, 29.4, 29.6, 29.7, 31.9, 34.5, 126.4, 126.5, 127.0, 127.3, 128.1, 128.6, 128.9, 129.5, 129.7, 137.8, 137.9, 139.1; MS *m/z* (rel intensity): 346 (M^+, 16), 205 (100), 129 (19), 91 (25), 43 (7). Anal. Calcd for $C_{26}H_{34}$: C, 90.11; N, 9.89. Found: C, 90.04; H, 10.09.

(3*E*,5*E*)-4-Decyl-1,8-diphenyl-3,5-octadiene ((3*E*)-2a). R_f=0.35 (hexane); bp 215-217 °C (bath temp, 0.40 Torr); IR (neat): 2922, 2852, 1730, 1603, 1496, 1454, 964, 743, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.3 Hz, 3H), 1.2-1.5 (m, 16H), 2.1-2.3 (m, 2H), 2.3-2.5 (m, 4H), 2.6-2.8 (m, 4H), 5.38 (t, *J*=6.7 Hz, 1H), 5.60 (dt, *J*=15.6, 6.7 Hz, 1H), 5.97 (d, *J*=15.6 Hz, 1H), 7.2-7.4 (m, 10 H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 27.0, 29.1, 29.4, 29.6, 29.7, 30.0, 30.2, 31.9, 34.9, 36.1, 36.2, 125.7, 125.8, 126.6, 128.2, 128.3, 128.4, 129.5, 133.9, 138.9, 142.0; MS *m/z* (rel intensity): 402 (M^+, 6), 311 (24), 207 (36), 143 (13), 117 (11), 95 (11), 91 (100), 67 (26). Anal. Calcd for $C_{30}H_{42}$: C, 89.49; H, 10.51. Found: C, 89.61; H, 10.56.

(3*Z*,5*E*)-4-Decyl-1,8-diphenyl-3,5-octadiene ((3*Z*)-2a). R_f=0.40 (hexane); bp 215-217 °C (bath temp, 0.40 Torr); IR (neat): 2922, 2852, 1730, 1497, 1273, 964, 743, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.87 (t, *J*=6.6 Hz, 3H), 1.2-1.6 (m, 16H), 2.1-2.3 (m, 2H), 2.4-2.6 (m, 4H), 2.6-2.8 (m, 4H), 5.28 (t, *J*=7.1 Hz, 1H), 5.71 (dt, *J*=15.7, 6.7 Hz, 1H), 6.29 (d, *J*=15.7 Hz, 1H), 7.2-7.4 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 29.0, 29.3, 29.6, 30.0, 31.9, 34.2, 35.2, 39.7, 125.6, 125.8, 126.0, 126.7, 128.2, 128.3, 128.4, 128.5, 129.3, 136.6; MS *m/z* (rel intensity): 402

(M^+, 10), 311 (19), 207 (27), 129 (11), 117 (9), 91 (100), 67 (22). Anal. Calcd for $C_{30}H_{42}$: C, 89.49; H, 10.51. Found: C, 89.60; H, 10.65.

(9*E*,11*E*)-10-Phenyl-9,11-icosadiene. R_f=0.78 (hexane); bp 165–167 °C (bath temp, 0.26 Torr); IR (neat): 2922, 2852, 1730, 1459, 1272, 965, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.1–1.6 (m, 24H), 2.12 (dt, *J*=7.0, 7.0 Hz, 2H), 2.28 (dt, *J*=7.0, 7.0 Hz, 2H), 5.41 (t, *J*=7.2 Hz, 1H), 5.52 (dt, *J*=15.6, 7.0 Hz, 1H), 6.49 (d, *J*=15.6 Hz, 1H), 7.2–7.5 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 28.9, 29.3, 29.4, 29.9, 31.9, 32.8, 126.5, 127.9, 129.5, 131.3, 131.7, 134.1, 139.0, 141.0; MS *m/z* (rel intensity): 354 (M^+, 52), 255 (49), 241, (95), 143 (100), 129 (59), 91 (77), 43 (48). Anal. Calcd for $C_{26}H_{42}$: C, 88.06; H, 11.94. Found: C, 88.12; H, 12.22.

(9*Z*,11*E*)-10-Phenyl-9,11-icosadiene. R_f=0.73 (hexane); bp 165–167 °C (bath temp, 0.26 Torr); IR (neat): 2922, 2852, 1731, 1465, 1272, 967, 699 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.1–1.5 (m, 24H), 1.88 (dt, *J*=7.6, 7.2 Hz, 2H), 2.0–2.1 (m, 2H), 5.11 (dt, *J*=15.6, 7.0 Hz, 1H), 5.58 (t, *J*=7.6 Hz, 1H), 6.23 (d, *J*=15.6 Hz, 1H), 7.1–7.2 (m, 2H), 7.3–7.5 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 28.1, 29.3, 29.4, 29.5, 29.6, 29.8, 31.9, 33.3, 126.5, 126.6, 127.8, 128.8, 130.9, 134.7, 139.4, 142.8; MS *m/z* (rel intensity): 354 (M^+, 40), 255 (51), 241 (77), 143 (100), 129 (44), 91 (61), 43 (43). Anal. Calcd for $C_{26}H_{42}$: C, 88.06; H, 11.94. Found: C, 87.77; 11.91.

(3*E*,5*E*)-4,5-Dipentyl-1,8-diphenyl-3,5-octadiene ((5*E*)-2b). R_f=0.30 (hexane); bp 170–172 °C (bath temp, 0.27 Torr); IR (neat): 2952, 2924, 2854, 1729, 1454, 1272, 744, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.87 (t, *J*=6.7 Hz, 6H), 1.1–1.4 (m, 12H), 2.0–2.2 (m, 4H), 2.38 (dt, *J*=7.0, 7.6 Hz, 4H), 2.68 (t, *J*=7.8 Hz, 4H), 5.37 (t, *J*=7.0 Hz, 2H), 7.2–7.5 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 28.0, 28.5, 30.3, 31.9, 36.3, 124.9, 125.7, 128.2, 128.5, 142.0, 142.2; MS *m/z* (rel intensity): 402 (M^+, 15), 311 (17), 207 (73), 117 (12), 91 (100), 67 (18), 43 (15).

Anal. Calcd for $C_{30}H_{42}$: C, 89.49; H, 10.51. Found: C, 89.64; H, 10.68.

(3*E*,5*Z*)-4,5-Dipentyl-1,8-diphenyl-3,5-octadiene ((5*Z*)-2b). R_f=0.40 (hexane); bp 170–172 °C (bath temp, 0.27 Torr); IR (neat): 2952, 2924, 2852, 1730, 1453, 1271, 743, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.86 (t, *J*=6.5 Hz, 3H), 0.88 (t, *J*=6.7 Hz, 3H), 1.1–1.4 (m, 12H), 1.9–2.1 (m, 4H), 2.3–2.5 (m, 4H), 2.6–2.8 (m, 4H), 4.97 (t, *J*=7.5 Hz, 1H), 5.18 (t, *J*=7.0 Hz, 1H), 7.2–7.4 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 27.8, 27.9, 28.9, 29.7, 31.1, 31.4, 32.1, 36.3, 36.9, 125.2, 125.6, 125.7, 127.2, 128.2, 128.4, 128.5, 139.1, 142.2, 142.5, 143.9; MS *m/z* (rel intensity): 402 (M^+, 14), 311 (16), 207 (71), 117 (8), 91 (100), 67 (10), 43 (10). Anal. Calcd for $C_{30}H_{42}$: C, 89.49; H, 10.51. Found: C, 89.55; H, 10.60.

(2*E*,4*E*)-4-Pentyl-1-phenyl-2,4-decadiene (3b) and **4-Pentyl-1-phenyl-3,5-decadiene (4b).** The two compounds (**3b**/**4b**=29/71) could not be separated. Bp 123–125 °C (bath temp, 0.12 Torr); IR (neat): 2954, 2924, 2856, 1605, 1496, 1466, 1455, 1378, 964, 744, 696 cm^{-1}; ^1H NMR ($CDCl_3$): 0.8–1.0 (m, 6H), 1.2–1.5 (m, 12H (**3b**)+10H (**4b**)), 2.0–2.3 (m, 4H), 2.43 (dt, *J*=7.2, 7.9 Hz, 2H (**4b**)), 2.68 (t, *J*=7.9 Hz, 2H (**4b**)), 3.43 (d, *J*=6.7 Hz, 2H (**3b**)), 5.36 (t, *J*=7.2 Hz, 1H), 5.57 (dt, *J*=15.6, 6.8 Hz, 1H (**4b**)), 5.69 (dt, *J*=16.1, 6.7 Hz, 1H(**3b**)), 5.92 (d, *J*=15.6 Hz, 1H (**4b**)), 6.01 (d, *J*=16.1, 1H (**3b**)), 7.2–7.4 (m, 5H); MS *m/z* (rel intensity): 284 (M^+, 30), 193 (82), 137 (23), 91 (100), 67 (53). Anal. Calcd. for $C_{21}H_{32}$: C, 88.66; H, 11.34. Found: C, 88.53; H, 11.58.

(*E*)-1-(1-Dodecenyl)cyclohexene (5). R_f=0.78 (hexane); bp 130–132 °C (bath temp, 0.30 Torr); IR (neat): 2952, 2924, 2854, 1733, 1466, 1273, 1136, 1073 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H), 1.2–1.6 (m, 14H), 1.4–1.8 (m, 6H), 2.0–2.2 (m, 6H), 5.53 (dt, *J*=15.6, 6.7 Hz, 1H), 5.62 (bs, 1H), 6.01 (d, *J*=15.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 22.7, 24.6, 25.8, 26.9, 29.3, 29.4, 29.5, 29.6, 29.7, 30.1, 31.9, 32.9, 126.9, 127.0, 133.3, 135.7; MS *m/z* (rel intensity): 248 (M^+, 98), 135 (95), 93 (88), 79 (93), 41 (100). Anal. Calcd for $C_{18}H_{32}$: C, 87.02; H,

12.98. Found: C, 86.93; H, 13.11.

(*E*)-1-Phenyl-4-pentadecen-3-ol (9a). To a stirring solution of $NbCl_5$ (1.1 g, 4.0 mmol) in a mixed solvent of DME and benzene (1:1, 10 mL) at 25 °C under an argon atmosphere was added zinc (0.39 g, 6.0 mmol), and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 0 °C a solution of 1-dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 0 °C for 1h. THF (6 mL) was added to the mixture. The reaction mixture was stirred at 25 °C for 15 min. Immediately after addition of 3-phenylpropanal (0.16 g, 1.2 mmol) at 25 °C (10 s), aqueous NaOH solution (15%, 4 mL) was introduced at 25 °C to quench the reaction. The whole mixture was stirred at 25 °C for an additional 1h. The deposited brown solid was removed by filtration with Hyfro-Super Cel and washed with ethyl acetate (3x5 mL). The organic extracts were dried over $MgSO_4$ and concentrated in *vacuo*. Purification of the crude product by column chromatography on silica gel gave 0.11 g (38%) of (*E*)-1-phenyl-4-pentadecen-3-ol along with 96 mg (24%) of 1,3-diene derivatives **2a** and 7 mg (4%) of 1-dodecene. **9a**: R_f=0.23 (ethyl acetate-hexane, 1:10); bp 140-142 °C (bath temp, 0.30 Torr); IR (neat): 3314, 2922, 2582, 1456, 1031, 968, 743, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H), 1.2-1.5 (m, 17H), 1.7-2.0 (m, 2H), 2.03 (dt, *J*=6.6, 6.4 Hz, 2H), 2.69 (dt, *J*=2.2, 7.8 Hz, 2H), 4.0-4.2 (m, 1H), 5.48 (dd, *J*=6.8, 15.4 Hz, 1H), 5.66 (dt, *J*=15.4, 6.6 Hz, 1H), 7.2-7.5 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 29.1, 29.2, 29.4, 29.5, 31.6, 31.8, 32.1, 38.7, 72.0, 125.5, 128.1, 128.2, 131.9, 132.7, 141.9; MS *m/z* (rel intensity): 284 (M^+-H_2O, 17), 143 (28), 91 (100), 81 (29), 67 (51). Anal. Calcd for $C_{21}H_{34}O$: C, 83.38; H, 11.33. Found: C, 83.18; H, 11.60. The content of deuterium in **9a-*d*** was determined by ^1H NMR analysis.

References and Notes

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(5) See Chapter 3 and references cited therein.

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(7) Fourfold excesses of low-valent niobium was required in the case of terminal alkynes because undesirable side reactions such as dimerization of the alkynes took place.

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(10) S. F. Pedersen reported one to one coupling reaction of alkynes and aldehydes leading to allylic alcohols by Nb(III) complexes. Abstracts of the 194th National Meeting of the American Chemical Society; New Orleans, 1987; Div. of Org. Chem., No. 218.

(11) See Chapter 2 on partial reduction of alkynes with the low-valent niobium.

CHAPTER 5

Regioselective Synthesis of 1-Naphthols from Alkynes and Phthalaldehyde Using Low-valent Tantalum or Niobium.

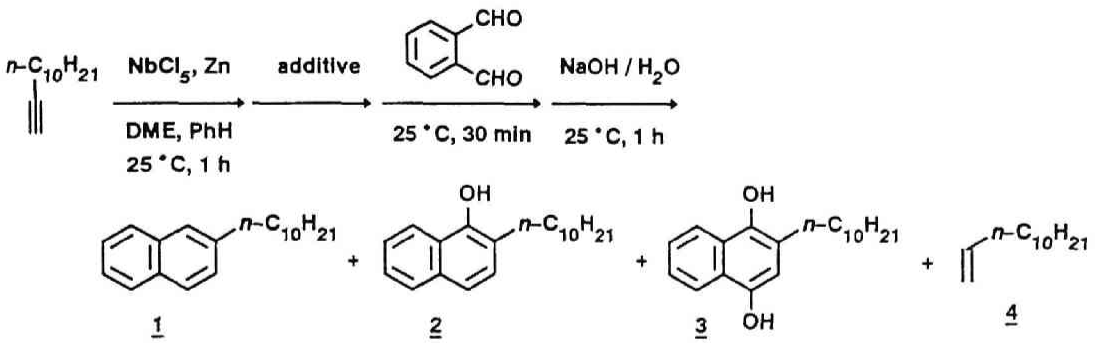
Treatment of tantalum (or niobium)-alkyne complexes, derived from alkynes and low-valent tantalum (niobium), with phthalaldehyde gives 2,3-disubstituted 1-naphthols in good to excellent yields.

Highly substituted phenol, naphtol, and hydroquinone derivatives are ubiquitous in many natural products.[1] Regioselective substitution on phenol and quinone skeletons provides an access to such compounds.[1] Cyclization[2] and annulation[3] methods from acyclic precursors have also been intensively studied, in particular, by means of organometallic compounds during the last decade. We disclose here a novel annulation method for the preparation of 2,3-disubstituted-1-naphthols from phthalaldehyde and alkynes mediated by low-valent tantalum or niobium.

Niobium-alkyne complexes[4] are generated *in situ* by reaction of alkynes with low-valent niobium derived from $NbCl_5$ and zinc.[5] Tantalum-alkyne complexes[6] have also been produced from alkynes and a combination of $TaCl_5$ and zinc by the analogous method of the low-valent niobium.[5,7] To examine the use of the metal-alkyne complexes as a cis vicinal alkene dianion synthon,[4b,5,7] phthalaldehyde, which has two formyl groups, was introduced to the reaction mixture of the metal-alkyne complexes.

Niobium-alkyne complexes react with 2 equiv of carbonyl compounds and successive deoxygenation produces 1,3-diene derivatives.[5c] Treatment of a niobium-1-dodecyne complex with phthalaldehyde under the same reaction conditions gave a mixture of three compounds having naphthalene skeleton **1**, **2**, **3**, and 1-dodecene **4** in 23%, 14%, 2%, and 24% yields, as shown in Table 1. Several additives were examined to obtain one of the naphthalene compounds in a selective manner. Addition of amines to the niobium-alkyne complexes increased the yield of 2-decyl-1-naphthol **2** and decreased that of 2-decylnaphthalene **1**. Among those amines examined, 2,6-lutidine gave the best result.

Table 1. Reaction of a Niobium–6–dodecyne Complex with Phthalaldehyde.[a]



Run	Additive	Equiv	Yields / %			
			1	**2**	**3**	**4**
1	THF	2	23	14	2	24
2	HMPA	2	8	50	11	27
3	Et_3N	2	4	45	7	11
4	pyridine	2	0	45	7	7
5	2,6–lutidine	2	0	53	5	22
6		3	0	59	4	14

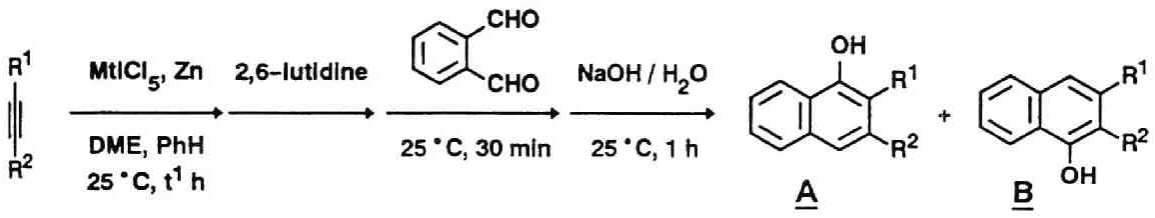
a) The reaction was conducted in a 1.0 mmol scale. Four mol of $NbCl_5$, 6.0 mol of zinc, 2.0 mol of phthalaldehyde was employed per mol of 1–dodecyne.

In contrast to the terminal alkynes, internal alkynes afforded 2,3–disubstituted–1–naphthol derivatives selectively without any additives. Tantalum–alkyne complexes, which were formed smoothly compared to the niobium cases,[5,7] have been found to react with phthalaldehyde to afford 1–naphthol derivatives.[5b] In both cases, pretreatment of the metal–alkyne complexes with 2,6–lutidine improved the yields of the 1–naphthol derivatives. Preparation of 1–naphthols from alkynes and phthalaldehyde is summarized in Table 2.

Because of the consumption of phthalaldehyde under the reaction conditions is very fast, 2–3 equiv of phthalaldehyde was employed. In the reaction of the other alkyne complex, 3 equiv of phthalaldehyde was used. Reactions between terminal alkynes and phthalaldehyde gave 2–substituted–1–naphthols regioselectively[8] and 3–substituted ones were not observed (runs 11 and 12). There is a tendency that bulky substituents occupy 3–position of the 2,3–disubstituted–1–naphthols in the case of unsymmetrically disubstituted alkynes especially when tantalum–alkyne complexes were employed (runs 5,6, and 8–10). One of the regioisomers was produced exclusively when the bulkiness of the substituent differs greatly from the other (runs 7, 13 and 14). The regiochemistries of **6**, **7**, and **8** (run 5,6,7) were confirmed by comparison with the authentic samples, which were prepared with $NbCl_3(DME)$.[4b] The authentic samples of 1–naphthols from phenyl substituted alkyne and phthalaldehyde were prepared by Semmelhack's method (runs 8, 9, and 10).[9] Trimethylsilyl–substituted–1–naphthol was desilylated smoothly with CF_3CO_2H[10] and its regiochemistry was ascertained by comparison with the product from the terminal alkyne.

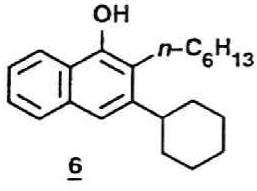
In 1989, Pedersen reported the synthesis of 1–naphthols from alkynes and phthalaldehyde promoted by $NbCl_3(DME)$.[4b] The reaction using a $NbCl_5$–Zn system gave almost the same regioselectivities. In contrast, tantalum–alkyne complexes reacted with phthalaldehyde under high regiocontrol (runs 5 and 9). Fast formation of tantalum–alkyne complexes compared to the niobium ones is worth noting.

Table 2. Preparation of 1-Naphthols by the Reaction of Phthalaldehyde with Tantalum (or Niobium)-Alkyne Complexes.



Run	R^1	R^2	Mtl[a]	t^1/h	Aldehyde / equiv	Yield[b] / %	A / B
1	n-C_5H_{11}	n-C_5H_{11}	Ta	0.5	2	84	--
2			Nb	10	2	93	--
3	Ph	Ph	Ta	6[c]	3	70	--
4		$-(CH_2)_{10}-$	Ta	0.5	4	70[d,e]	--
5	n-C_6H_{13}	c-C_6H_{11} (5)	Ta	2	3	85[f]	>99 / <1
6			Nb	11	3	84[g]	67 / 33
7	n-C_7H_{15}	t-Bu	Ta	4.5	3	71[f,h]	>99 / <1
8	Me	Ph	Ta	0.5	3	72[d]	71 / 29[i]
9	n-C_6H_{13}	Ph	Ta	2	3	71	75 / 25
10			Nb	12	3	83	55 / 45
11	n-$C_{10}H_{21}$	H	Nb	1	3	59[f]	>99 / <1
12	Ph	H	Nb	2	3	31[f]	>99 / <1
13	n-$C_{10}H_{21}$	Me_3Si	Ta	1.5	3	88[f,j]	>99 / <1
14	Ph	Me_3Si	Ta	7	3	64[f,j]	>99 / <1

a) Ta: A tantalum-alkyne complex, prepared by treatment of an alkyne (1.0 mmol) with a low-valent tantalum derived from $TaCl_5$ (2.0 mmol) and zinc (3.0 mmol), was treated with 2,6-lutidine (4.0 mmol) and phthalaldehyde (3.0 mmol). Nb: Low-valent niobium was generated upon treatment of $NbCl_5$ (4.0 mmol) with zinc (6.0 mmol) and employed instead of the low-valent tantalum. b) Isolated yields. c) Complexation of diphenylacetylene with the low-valent tantalum was conducted at 50 °C. d) HMPA (2.0 mmol) was used instead of 2,6-lutidine. e) Cyclododecene was obtained in 21% yield. f) The other regioisomer was not observed. g) Reaction of 5 with $NbCl_3$(DME) produced the same regioisomer 6 as a main product (6/7=86/14) in our hands. h) Four mmol of $TaCl_5$ and 6.0 mmol of zinc were employed. i) See ref. 9. j) Regiochemistry was ascertained by desilylation with CF_3CO_2H (ref. 10).



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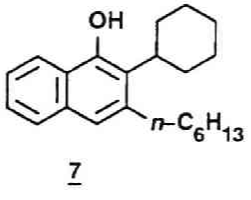
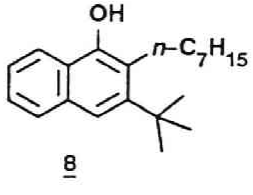


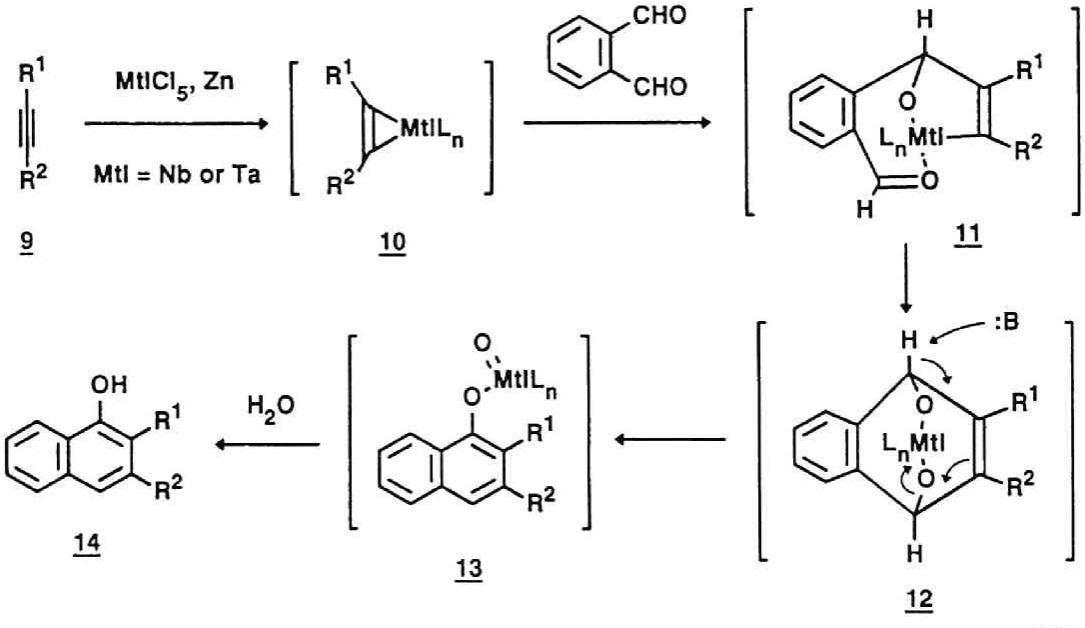
7



8

Plausible mechanism for the formation of 1-naphthol **14** is shown in Scheme 1. Low-valent tantalum (or niobium), generated from $TaCl_5$ ($NbCl_5$) and zinc, reacts with an alkyne **9** to produce a metal-alkyne complex **10**. Insertion of a formyl group into a metal-carbon bond of the complex **10** gives **11**. Internal coordination of the second formyl group at the suitable position of **11** facilitates the second insertion reaction leading to **12**. Elimination of a metaloxy group at benzylic position of **12** takes place in cooperation with proton abstraction by the hindered base to generate **13**, which affords 1-naphthol **14** after aqueous workup. Strong affinity of Mtl-O bond (Mtl = Ta or Nb)[11] and aromatic stabilization can be the driving force of the elimination.

Scheme 1



Since substitution reactions of trimethylsilyl (Me_3Si),[12] diethoxyphosphoryloxy ($(EtO)_2P(O)O$),[13] and trifluoromethanesulfonyloxy (TfO) groups[14] attached on aromatic rings are known to proceed smoothly under palladium or nickel catalysis, this method provides new access of substituted naphthalene derivatives.

Experimental Section

General Procedure for the Synthesis of 1-Naphthols with $NbCl_5$-Zn. In a 50-ml reaction flask was placed $NbCl_5$ (1.1 g, 4.0 mmol) under an argon atmosphere. To the salt were added at 25 °C benzene (10 mL) and DME (10 mL) successively. Zinc dust (0.20 g, 3.0 mmol) was added to a stirring pale yellow solution of $TaCl_5$ in DME and benzene (1:1, 20 mL) at 25 °C, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned from brown to dark brown with slightly exothermic process. To the mixture was added at 25 °C a solution of an alkyne (1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C. After consumption of the alkyne was confirmed by TLC, 2,6-lutidine (0.94 mL, 8.0 mmol) was added to the mixture. After the reaction mixture was stirred at 25 °C for 20 min, a solution of phthalaldehyde (0.40 g, 3.0 mmol) in DME and benzene (1:1, 2 mL) was added to the mixture, and the resulting mixture was stirred at 25 °C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for additional 1 h. The deposited solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The filtrate and washings were concentrated *in vacuo*. Resulting viscous solid was extracted well with hexane (5x5 mL), and the extracts were dried over Na_2SO_4 and concentrated *in vacuo* again. Purification by column chromatography on silica gel gave 1-naphthol.

General Procedure for the Synthesis of 1-Naphthols with $TaCl_5$-Zn. In a 50-ml reaction flask was placed $TaCl_5$ (0.72 g, 2.0 mmol) under an argon atmosphere. To the salt were added at 25 °C benzene (10 mL) and DME (10 mL) successively. Zinc dust (0.20 g, 3.0 mmol) was added to a stirring pale yellow solution of $TaCl_5$ in DME and benzene (1:1, 20 mL) at 25 °C, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned to greenish dark blue

with slightly exothermic process. To the mixture was added at 25 °C a solution of an alkyne (1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C. After consumption of the alkyne was confirmed by TLC, 2,6-lutidine (0.47 mL, 4.0 mmol) was added to the mixture. After the reaction mixture was stirred at 25 °C for 20 min, a solution of phthalaldehyde (0.40 g, 3.0 mmol) in DME and benzene (1:1, 2 mL) was added to the mixture, and the resulting mixture was stirred at 25 °C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for additional 1 h. The deposited solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The filtrate and washings were concentrated *in vacuo*. Resulting viscous solid was extracted well with hexane (5x5 mL) and the extracts were dried over Na_2SO_4 and concentrated *in vacuo* again. Purification by column chromatography on silica gel gave 1-naphthol.

2,3-Dipentyl-1-naphthol. R_f=0.53 (ethyl acetate-hexane, 1:10); Bp 151-153 °C (bath temp, 0.20 Torr); IR (neat): 3578, 2952, 2928, 2856, 1572, 1501, 1459, 1384, 1248, 1198, 1114, 744 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.92 (t, *J*=7.0 Hz, 6H), 1.4-1.6 (m, 12H), 2.7-2.8 (m, 4H), 5.14 (s, 1H), 7.26 (d, *J*=2.6 Hz, 1H), 7.4-7.5 (m, 2H), 7.7-7.8 (m, 1H), 8.0-8.1 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 26.2, 29.7, 31.0, 32.0, 32.2, 33.5, 119.8, 120.6, 121.5, 122.9, 124.4, 125.4, 127.1, 132.8, 140.0, 148.3; MS *m/z* (rel intensity): 356 (M^+-H+Me_3Si, 89), 285 (59), 243 (82), 171 (79), 73 (100), 68 (61). Anal. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92. Found: C, 84.21; H, 10.13.

2,3-Diphenyl-1-naphthol.[4b] R_f=0.38 (ethyl acetate-hexane, 1:10); ^1H NMR ($CDCl_3$): δ 5.61 (s, 1H), 7.0-7.3 (m, 10H), 7.4-7.5 (m, 3H), 7.7-7.8 (m, 1H), 8.1-8.2 (m, 1H).

Cyclododeceno[b]-1-naphthol. The compound was prepared by using HMPA instead of 2,6-lutidine. R_f=0.65 (ethyl acetate-hexane, 1:10); bp 180-182

°C (bath temp, 0.29 Torr); IR (neat): 3126, 3046, 1729, 1567, 1286, 1168, 1095, 873, 742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4–1.7 (m, 12H), 1.7–1.9 (m, 4H), 2.7–2.9 (m, 4H), 5.15 (s, 1H), 7.1–7.2 (m, 1H), 7.3–7.5 (m, 2H), 7.7–7.8 (m, 1H), 8.0–8.1 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 22.6, 22.9, 23.9, 25.9, 26.7, 26.8, 27.2, 27.6, 30.1, 31.0, 120.2, 120.6, 121.4, 122.7, 124.4, 125.5, 127.0, 132.8, 140.7, 148.8; MS *m/z* (rel intensity): 354 (M^+–H+Me_3Si, 40), 75 (25), 73 (57), 68 (100), 41 (83). Anal. Calcd for $C_{20}H_{26}O$: C, 85.06; H, 9.28. Found: C, 84.96; H, 9.46.

3–Cyclohexyl–2–hexyl–1–naphthol (6). R_f=0.55 (ethyl acetate–hexane, 1:10); Bp 170–172 °C (bath temp, 0.25 Torr); IR (neat): 3578, 2922, 2848, 1572, 1500, 1449, 1387, 1227, 1102, 743 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.91 (t, *J*=6.2 Hz, 3H), 1.2–1.7 (m, 14H), 1.8–2.0 (m, 4H), 2.7–2.9 (m, 3H), 5.15 (s, 1H), 7.4–7.5 (m, 3H), 7.7–7.8 (m, 1H), 8.0–8.1 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 25.8, 26.3, 27.3, 29.6, 30.3, 31.6, 34.9, 40.3, 117.1, 120.5, 121.2, 122.7, 124.4, 125.3, 127.3, 132.9, 145.1, 148.0; MS *m/z* (rel intensity): 382 (M^+–H+Me_3Si, 100), 311 (13), 243 (30), 231 (13), 81 (17), 73 (55), 43 (10), 41 (9). Anal. Calcd for $C_{22}H_{30}O$: C, 85.11; H, 9.74. Found: C, 85.13; H, 9.71. The regiochemistry was confirmed by comparison with the authentic sample, which was prepared according to the Petersen's method.[4b]

2–Cyclohexyl–3–hexyl–1–naphthol (7). R_f=0.41 (ethyl acetate–hexane, 1:10); Bp 170–172 °C (bath temp, 0.25 Torr); IR (neat): 3576, 2922, 2850, 1573, 1500, 1449, 1387, 1226, 1103, 744 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.91 (t, *J*=6.8 Hz, 3H), 1.2–1.7 (m, 12H), 1.7–2.0 (m, 4H), 2.1–2.3 (m, 2H), 2.77 (t, *J*=7.6 Hz, 2H), 2.9–3.1 (m, 1H), 5.32 (s, 1H), 7.25 (d, *J*=2.6 Hz, 1H), 7.4–7.5 (m, 2H), 7.7–7.8 (m, 1H), 8.0–8.1 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 26.3, 27.6, 29.3, 30.9, 31.6, 31.7, 35.4, 39.1, 119.8, 120.7, 124.0, 124.5, 125.4, 125.8, 126.0, 127.1, 132.7, 140.2; MS *m/z* (rel intensity): 382 (M^+–H+Me_3Si, 100), 297 (14), 255 (12), 243 (9), 229 (7), 73 (53), 43 (12), 41 (8). Anal. Calcd for $C_{22}H_{30}O$: C, 85.11; H, 9.74.

Found: C, 85.07; H, 9.58. The regiochemistry was confirmed by comparison with authentic sample.[4b]

3-*tert*-Butyl-2-heptyl-1-naphthol (8). R_f=0.68 (ethyl acetate-hexane, 1:10); Bp 150-152 °C (bath temp, 0.24 Torr); IR (neat): 3568, 2954, 2924, 2854, 1728, 1466, 1381, 1281, 1201, 1105, 743 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8-1.0 (m, 3H), 1.1-1.8 (m, 10H), 1.49 (s, 9H), 2.9-3.1 (m, 2H), 5.26 (s, 1H), 7.3-7.6 (m, 3H), 7.7-7.8 (m, 1H), 7.9-8.1 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 28.8, 29.2, 29.4, 29.6, 30.5, 31.8, 117.4, 120.1, 122.4, 122.9, 124.9, 125.5, 127.9, 132.3, 146.7, 149.7; MS *m/z* (rel intensity): 370 (M^+-H+Me_3Si, 100), 285 (20), 73 (65), 57 (17), 43 (10). Anal. Calcd for $C_{21}H_{30}O$: C, 84.51; H, 10.13. Found: C, 84.40; H, 10.39. The regiochemistry was confirmed by comparison with the authentic sample.[4b]

2-Methyl-3-phenyl-1-naphthol. The compound was prepared by using HMPA instead of 2,6-lutidine. R_f=0.32 (ethyl acetate-hexane, 1:10); Bp 140-142 °C (bath temp, Torr); IR (neat): 3426, 2924, 1724, 1494, 1377, 1260, 702 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.26 (s, 3H), 5.29 (s, 1H), 7.3-7.5 (m, 8H), 7.7-7.8 (m, 1H), 8.1-8.2 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 13.2, 115.3, 120.9, 121.1, 123.3, 125.3, 125.8, 126.9, 127.6, 128.0, 129.4, 132.4, 141.4, 141.7, 148.9; MS *m/z* (rel intensity): 306 (M^+-H+Me_3Si, 100), 291 (21), 276 (8), 261(9), 215 (11), 73 (49), 45 (10). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.03; H, 6.06. The regiochemistry was confirmed by comparison with the authentic sample, which was prepared according to the Semmelhack's method.[9]

3-Methyl-2-phenyl-1-naphthol. R_f=0.58 (ethyl acetate-hexane, 1:10); Bp 140-142 °C (bath temp, 0.25 Torr); IR (neat): 2524, 2922, 1728, 1572, 1390, 1289, 1071, 703 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.19 (s, 3H), 5.26 (s, 1H), 7.3-7.6 (m, 8H), 7.7-7.8 (m, 1H), 8.2-8.3 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 21.2, 119.7, 122.3, 122.5, 122.6, 124.6, 126.4, 126.7, 128.3, 129.6, 130.6, 133.8, 134.5, 135.4, 148.0;

MS *m/z* (rel intensity): 306 (M^+–H+Me_3Si, 100), 292 (12), 291 (34), 176 (16), 275 (7), 261 (15), 73 (20). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.00; H, 5.85. The regiochemistry was confirmed by comparison with authentic sample.[9]

2-Hexyl-3-phenyl-1-naphthol. The compound was prepared by using HMPA instead of 2,6-lutidine. R_f=0.57 (ethyl acetate–hexane, 1:10); Bp 180–182 °C (bath temp, 0.28 Torr); IR (neat): 3452, 2952, 2924, 2852, 1593, 1388, 1255, 1105, 764, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.74 (t, *J*=6.0 Hz, 3H), 1.0–1.2 (m, 6H), 1.3–1.5 (m, 2H), 2.61 (t, *J*=8.1 Hz, 2H), 5.22 (s, 1H), 7.2–7.5 (m, 8H), 7.7–7.8 (m, 1H), 8.0–8.1 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.4, 27.0, 29.3, 29.7, 31.3, 120.9, 121.3, 123.5, 125.2, 125.9, 126.9, 127.6, 127.9, 129.3, 132.4, 141.4, 142.0, 148.6; MS *m/z* (rel intensity): 376 (M^+–H+Me_3Si, 100), 306 (22), 305 (90), 215 (13), 73 (92), 43 (8). Anal. Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.92; H, 7.94. The regiochemistry was confirmed by comparison with the authentic sample.[9]

3-Hexyl-2-phenyl-1-naphthol. R_f=0.71 (ethyl acetate–hexane, 1:10); Bp 180–182 °C (bath temp, 0.28 Torr); IR (neat): 3540, 2952, 2924, 2854, 1726, 1571, 1382, 1287, 1063, 747, 704, 664 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.81 (t, *J*=6.5 Hz, 3H), 1.1–1.4 (m, 6H), 1.3–1.5 (m, 2H), 2.49 (t, *J*=7.8 Hz, 2H), 5.22 (s, 1H), 7.3–7.6 (m, 8H), 7.7–7.8 (m, 1H), 8.2–8.3 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.5, 29.1, 30.7, 31.5, 33.9, 119.0, 122.3, 122.5, 124.6, 126.4, 126.9, 128.3, 129.4, 130.9, 133.9, 125.2, 139.3, 148.0; MS *m/z* (rel intensity): 376 (M^+–H+Me_3Si, 100), 307 (14), 305 (28), 215 (11), 73 (73), 43 (17). Anal. Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.58; H, 8.05. The regiochemistry was confirmed by comparison with authentic sample.[9]

2-Decyl-1-naphthol (2). R_f=0.53 (ethyl acetate–hexane, 1:10); Bp 155–157 °C (bath temp, 0.27 Torr); IR (neat): 3574, 2954, 2924, 2850, 1576, 1467,

1391, 1283, 803, 743, 663 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.87 (t, *J*=6.8 Hz, 3H), 1.2–1.5 (m, 14H), 1.6–1.8 (m, 2H), 2.74 (t, *J*=7.7 Hz, 2H), 5.14 (s, 1H), 7.26 (d, *J*=2.4 Hz, 1H), 7.2–7.4 (m, 3H), 7.8–7.9 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 29.3, 29.6, 30.0, 31.9, 120.2, 121.0, 121.3, 124.4, 125.2, 125.4, 127.6, 128.1, 133.3, 148.0; MS *m/z* (rel intensity): 356 (M^+–H+Me_3Si, 98), 229 (71), 205 (100), 91 (28), 73 (57), 43 (30). Anal. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92. Found: C, 84.41; H, 9.99. The regiochemistry was confirmed by comparison with commercially available 2–methyl–1–naphthol.

2–Phenyl–1–naphthol.[8] R_f=0.47 (ethyl acetate–hexane, 1:10); ^1H NMR ($CDCl_3$): δ 5.85 (s, 1H), 7.4–7.6 (m, 9H), 7.8–7.9 (m, 1H), 8.3–8.4 (m, 1H).

2–Decyl–3–(trimethylsilyl)–1–naphthol. R_f=0.55 (ethyl acetate–hexane, 1:10); Bp 149–151 °C (bath temp, 0.18 Torr); IR (neat): 3420, 2950, 2922, 2850, 1438, 1379, 836, 749 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.39 (s, 9H), 0.88 (t, *J*=6.2 Hz, 3H), 1.1–1.7 (m, 16H), 2.8–3.0 (m, 2H), 5.14 (s, 1H), 7.4–7.6 (m, 2H), 7.61 (bs, 1H), 7.8–7.9 (m, 1H), 8.1–8.2 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 0.7, 14.1, 22.7, 29.4, 29.6, 30.3, 30.4, 31.1, 31.9, 120.6, 124.9, 125.3, 125.8, 126.1, 127.9, 132.7, 138.2, 148.2; MS *m/z* (rel intensity): 428 (M^+–H+Me_3Si, 67), 355 (9), 301 (34), 73 (100), 43 (9). Anal. Calcd for $C_{23}H_{36}O$: C, 77.46; H, 10.17. Found: C, 77.35; H, 10.39. This sample was desilylated with CF_3CO_2H and its regiochemistry was ascertained by comparison with the product from 1–dodecyne.

2–Phenyl–3–(trimethylsilyl)–1–naphthol. R_f=0.63 (ethyl acetate–hexane, 1:10); Bp 155–157 °C (bath temp, 0.27 Torr); IR (neat): 3496, 3042, 1580, 1444, 1246, 837, 752 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.12 (s, 9H), 5.30 (s, 1H), 7.4–7.6 (m, 2H), 7.5–7.7 (m, 5H), 7.81 (bs, 1H), 7.9–8.0 (m, 1H), 8.3–8.4 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 0.5, 122.3, 124.2, 126.0, 126.1, 126.3, 127.0, 127.6, 128.5, 129.0, 131.4, 133.5, 137.0, 137.6, 147.5; MS *m/z* (rel intensity): 364 (M^+–H+Me_3Si, 100), 349 (27), 261 (84), 259 (29), 73 (74), 45 (23). Anal. Calcd for $C_{19}H_{20}OSi$: C,

78.03; H, 6.89. Found: C, 78.07; H, 6.87. This sample was desilylated with CF_3CO_2 and its regiochemistry was ascertained by comparison with the product from phenylacetylene.

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CHAPTER 6

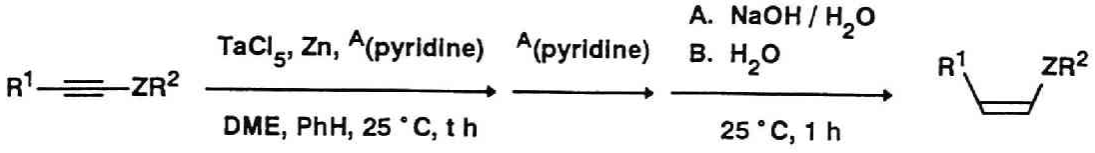
Regio- and Stereoselective Reaction of Tantalum-(1-Alkylthio-1-alkyne) Complexes with Carbonyl Compounds.

Treatment of 1-alkynyl methyl sulfides with low-valent tantalum derived from $TaCl_5$ and Zn in DME and benzene produces tantalum-alkyne complexes (not isolated), which react *in situ* with carbonyl compounds at 2-position of the alkenyl sulfides to give (*E*)-3-methylthio-2-propen-1-ol derivatives in a regio- and stereoselective manner.

Because a variety of substituted acetylenes are readily accessible as starting materials, carbo-[1] and hydrometalation[2] of alkynes provide a convenient route for stereoselective construction of tetra- and trisubstituted ethenes. In such reactions, hetero-atom substituents on acetylenic triple bonds sometimes play an important role to direct the regiochemistry.[3,4] For example, hydroalumination of 1-alkynyl sulfoxides produces α-aluminium-substituted 1-alkenyl sulfoxides because of the strong electron withdrawing effect of the sulfinyl group.[3] The alternative route for stereoselective synthesis of alkenes is the utilization of metal-alkyne complexes as a key intermediate.[5-8] One of the typical examples of hetero-atom substituent effects is observed in zirconocene case.[6f] Alkylthio groups on acetylenes stabilize zirconocene-alkyne complexes significantly and the groups can be used to control the regiochemistry in subsequent coupling with other alkynes. We recently found a novel access to tantalum-alkyne complexes by means of low-valent tantalum.[5] The formed tantalum-alkyne complexes are used *in situ* to add to carbonyl compounds to furnish (*E*)-allylic alcohols stereoselectively. To examine the applicability of the method and effects of hetero-atom substituents on acetylenes, sulfur substituted acetylenes are prepared and employed in the reaction mediated by the low-valent tantalum.

Formation of tantalum-alkyne complexes from 1-alkynyl sulfides[9] proceeded faster than that of tantalum-dialkyl acetylene complexes.[5c] 1-Alkenyl sulfides were produced after alkaline workup. Pretreatment of the low-valent tantalum with pyridine before addition of alkynes prevented the formation of 1-chloro-1-alkenyl sulfides as byproducts. Although *Z*-isomers were obtained predominantly, the *Z*/*E* selectivities of the produced 1-alkenyl sulfides varied with the hydrolytic conditions. Addition of 20 equiv of pyridine before alkaline workup was found to suppress the isomerization, and (*Z*)-1-alkenyl sulfides were obtained under high stereocontrol (Table 1). Complexation of 1-alkynyl sulfone[10] with the low-valent

Table 1. Preparation of (*Z*)-Alkenyl Sulfides and Sulfones by Hydrolysis of the Corresponding Tantalum-Alkyne Complexes.

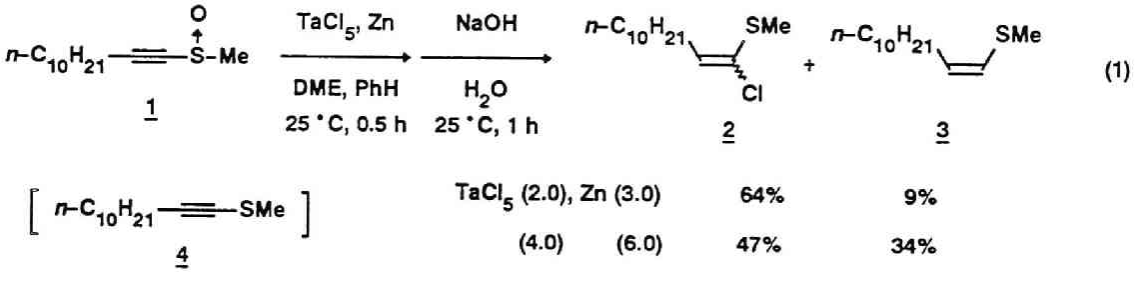


Run	R^1	ZR^2	Method[a]	t / h	Yields / %[b]	Z / E[c]
1	n-$C_{10}H_{21}$	SMe	A	0.75	97	98 / 2
2		SPh	A	1	96	93 / 7
3	c-C_6H_{11}	SMe	A	0.5	75	98 / 2
4	Ph	SMe	A	0.5	91	98 / 2
5	n-$C_{10}H_{21}$	SO_2Me	B	2.5	72[d]	100 / 0
6		SO_2Ph	B	22	69[d]	100 / 0
7	c-C_6H_{11}	SO_2Me	B	2.5	68[d]	100 / 0

a) Reactions were performed on a 1.0 mmol scale at 25 °C. Method A: Two mmol of $TaCl_5$, 3.0 mmol of zinc, and 1.0 mmol of pyridine were employed. Additional pyridine (20 mmol) was introduced to the reaction mixture before hydrolysis with a NaOH solution (15%, 2 mL). Method B: Three mmol of $TaCl_5$, 4.5 mmol of zinc were employed. The reaction was quenched with water (3 mL). b) Isolated yields. c) Geometric purity was ascertained by ^1H or ^{13}C NMR and/or capillary GLPC analysis. d) Ref. 13.

tantalum proceeded more slowly than 1-alkynyl sulfides under the same conditions.[5e] Three equiv of the low-valent tantalum was required to complete the complexation. The reaction mixture of tantalum-1-alkynyl sulfone complexes were quenched with water in order to suppress the isomerization of the double bond under basic conditions.[11] (*Z*)-1-Alkenyl sulfones were produced predominantly and the chlorinated products were not observed (runs 5-7).

In contrast to the 1-alkynyl sulfides and sulfones, treatment of 1-alkynyl sulfoxide **1** with the $TaCl_5$-Zn system did not give the corresponding 1-alkenyl sulfoxide but afforded a mixture of 1-chloro-1-alkenyl sulfide **2** and (*Z*)-1-alkenyl sulfide **3** (Eq. 1). Both 1-chloro-1-alkenyl sulfide **2** and 1-alkenyl sulfide **3** could stem from 1-dodecynyl methyl sulfide **4**, because (i) treatment of the sulfide **4** with $TaCl_5$ in the absence of pyridine at 25 °C for 2 h afforded 1-chloro-1-dodecenyl methyl sulfide **2** in 50% yield and (ii) the yield of **2** decreased and that of **3** increased with increasing the amounts of low-valent tantalum. Because of the strong oxophilicity of tantalum, deoxygenation of the 1-alkynyl sulfoxide into the corresponding sulfide could occur prior to the formation of a tantalum complex of sulfoxide **1**.

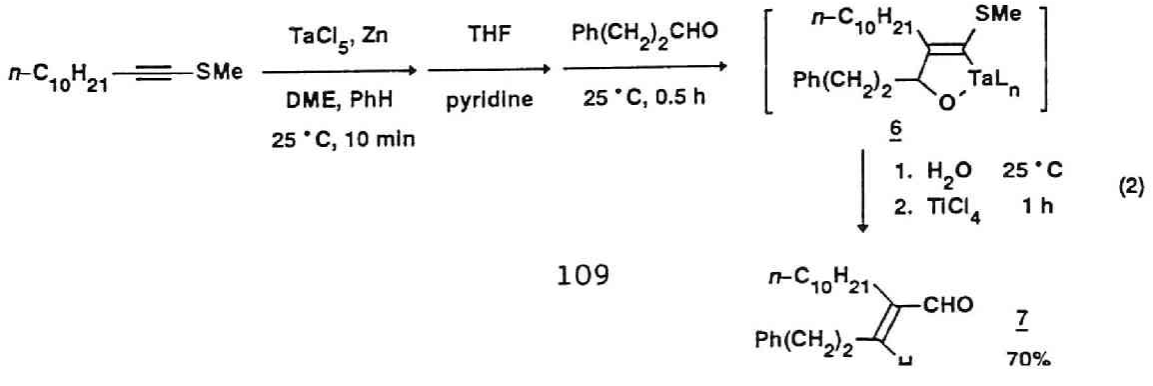


Addition of 20 equiv of pyridine prior to treatment of 1-alkynyl sulfides retarded the reaction between the formed tantalum-1-alkyne complexes and carbonyl compounds and unreacted 1-alkenyl sulfides remained. Therefore, pyridine was not used before addition of the 1-alkenyl sulfides in the case of the reaction between tantalum-alkyne complexes and carbonyl compounds. Although

substantial amounts (15–20%) of 1–chloro–1–alkenyl sulfides **2** was obtained as a byproduct, allylic alcohol **5** was produced regioselectively in 73% yield. The result shows sharp contrast to a zirconocene–(1–methylthio–1–alkyne) complex, which adds to a carbonyl compound to give two regioisomeric allylic alcohols in almost 1 to 1 ratio.[6f] Other results are shown in Table 2. Regioselectivities depended on the substituents on sulfur. Lower selectivities (**A**/**B**) were observed when 1–phenylthio–1–alkyne was employed (runs 2 and 5).

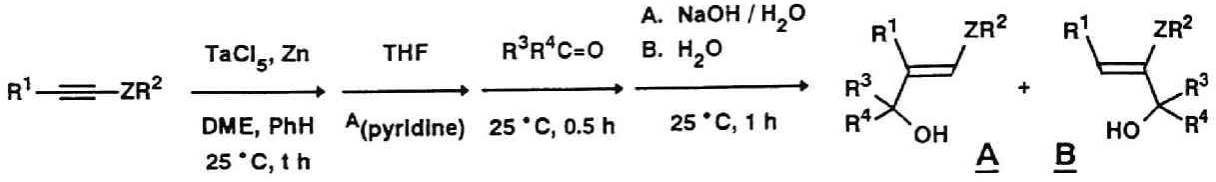
Tantalum–alkyne complexes derived from 1–alkynyl sulfones reacted with carbonyl compounds under the same conditions and two regioisomeric allylic alcohols were produced by addition at α– or β–positions of the starting sulfones were obtained except in the case of cyclohexanone (runs 10–14). Although the structure of the tantalum–alkyne complexes derived from sulfur–substituted alkynes and the $TaCl_5$–Zn system is not characterized, the regioselectivities are varied with steric and electronic effects[5g] of the substituents on acetylenes. The tantalum–1–alkyne complexes from 1–alkynyl methyl sulfides reacted with the carbonyl compound at only β–position of the starting sulfide group due to the electron–donating nature of the methylthio group. Phenylthio group having weaker electron–donating nature showed lower regioselectivity of the reaction (runs 2 and 5). The electron–withdrawing effect of sulfonyl group influence the regioselectivity to increase α–adducts of alkynyl sulfones with carbonyl compounds (runs 10–14).

Acidic hydrolysis of a tantalum–(1–methylthio–1–dodecyne) complex **6** proceeded smoothly with $TiCl_4$, and an *E*–isomer of α,β–unsaturated aldehyde **7** was produced exclusively in 70% yield (Eq. 2).[12]



(2)

Table 2. Reactions of Alkynyl Sulfides and Sulfones with Carbonyl Compounds by Means of a $TaCl_5$–Zn System.



Run	R^1	ZR^2	R^3	R^4	Method[a]	t / h	Yields / %[b]	A / B[c]
1	n-$C_{10}H_{21}$	SMe	$Ph(CH_2)_2$	H	A	0.2	73 (5)	>99 / <1
2		SPh			A	0.5	85	77 / 23
3		SMe	c-C_6H_{11}	H	A	0.2	74	>99 / <1
4			$-(CH_2)_5-$		A	0.2	77	>99 / <1
5		SPh			A	0.5	75	85 / 15
6	c-C_6H_{11}	SMe	$Ph(CH_2)_2$	H	A	0.2	68	>99 / <1
7			$-(CH_2)_5-$		A	0.2	70	>99 / <1
8	Ph	SMe	$Ph(CH_2)_2$	H	A	0.5	64	>99 / <1
9			$-(CH_2)_5-$		A	0.5	54	>99 / <1
10	n-$C_{10}H_{21}$	SO_2Me	$Ph(CH_2)_2$	H	B	2.5	54[d]	54 / 46
11		SO_2Ph			B	21	43[d]	28 / 72
12		SO_2Me	c-C_6H_{11}	H	B	2.5	46[d]	65 / 35
13			$-(CH_2)_5-$		B	2.5	62[d,e]	>99 / <1
14	c-C_6H_{11}	SO_2Me	$Ph(CH_2)_2$	H	B	2.5	59[d]	39 / 61

a) Reactions were performed on a 1.0 mmol scale at 25 °C. Method A: Two mmol of $TaCl_5$, 3.0 mmol of zinc, and 4.0 mmol of pyridine were employed. The reaction mixture was hydrolyzed with a 15% NaOH solution. Method B: Three mmol of $TaCl_5$ and 4.5 mmol of zinc were employed. Pyridine was not added to the reaction mixture. The reaction was quenched with water (3 mL). b) Isolated yields. c) The isomer ratios were determined by ^1H and ^{13}C NMR analysis. d) Ref. 13. e) Four mmol of cyclohexanone was used.

Experimental Section

Preparation of Surfur-substituted Acetylenes. Sulfur-substituted acetylenes were prepared according to the standard procedure in ref. 9.

1-Methylthio-1-dodecyne. To a stirring solution of 1-dodecyne (17 g, 100 mmol) in THF (200 mL) at 0 °C under an argon atmosphere was added butyllithium (75 mL of 1.6 M hexane solution, 120 mmol) dropwise over a period of 30 min. After the reaction mixture was stirred at 0 °C for 20 min, dimethyl disulfide (12 g, 130 mmol) was added to the mixture; the resulting mixture was stirred at 0 °C for an additional 2 h. The mixture was poured into ice-cold water and extarcted with hexane. The organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Distillation of the crude product gave 18 g (85%) of 1-methylthio-1-dodecyne. Bp 98-100 °C (bath temp. 0.20 Torr); IR (neat): 2924, 2852, 1730, 1465, 1313, 1272 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H), 1.2-1.4 (m, 14H), 1.4-1.6 (m, 2H), 2.28 (t, *J*=6.9 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 13.8, 19.0, 19.8, 22.5, 28.7, 29.0, 29.2, 29.4, 31.8, 69.7, 92.8; MS *m/z* (rel intensity): 212 (M^+, 16), 197 (18), 127 (21), 87 (100), 67 (42). Anal. Calcd for $C_{13}H_{24}S$: C, 73.51; H, 11.39. Found: C, 73.72; H, 11.69.

1-Phenylthio-1-dodecyne. The title compound was prepared in 60% yield from 1-dodecyne and diphenyl disulfide in the similar manner described above. Bp 156-158 °C (bath temp. 0.40 Torr); IR (neat): 2922, 2852, 1729, 1583, 1479, 1024, 735, 686 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H), 1.2-1.5 (m, 14H), 1.5-1.7 (m, 2H), 2.45 (t, *J*=6.9 Hz, 2H), 7.2-7.5 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 20.3, 22.6, 28.6, 28.9, 29.1, 29.3, 29.5, 31.9, 64.5, 100.0, 125.6, 125.9, 128.9, 133.8; MS *m/z* (rel intensity): 274 (M^+, 71), 190 (46), 149 (100), 103 (76), 81 (84). Anal. Calcd for $C_{18}H_{26}S$: C, 78.77; H, 9.55. Found: C, 78.94; H, 9.66.

1-Cyclohexyl-2-methylthioethyne. To the solution of 1,1-dibromo-2-cyclohexylethene[14] (18 g, 66mmol) in THF (300 mL) under an argon atmosphere at -78 °C, was added butyllithium (83mL of 1.6 M hexane solution, 132 mmol) dropwise over a period of 20 min. After stirred at -78 °C for 2 h, the reaction mixture was warmed to 25 °C and stirred at 25 °C for 1 h. A solution of dimethyl disulfide (8.1 g, 86 mmol) was added to the reaction mixture at 0 °C. The mixture was stirred at 0 °C for 30 min and 25 °C for 30 min. The mixture was poured into ice-cold water, extracted with hexane, and washed with brine. The organic extracts were dried over $MgSO_4$ and concentrated in *vacuo*. Distillation of the crude product gave 8.3 g (82%) of 1-cyclohexyl-2-methylthioethyne as a colorless liquid. Bp 67-69 °C (bath temp. 1.0 Torr); IR (neat): 2926, 2850, 1730, 1448, 1311, 973 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.2-1.7 (m, 6H), 1.6-1.9 (m, 4H), 2.35 (s, 3H), 2.4-2.5 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 19.3, 24.7, 25.7, 30.2, 32.6, 69.8, 96.9; MS *m/z* (rel intensity): 154 (M^+, 100), 139 (81), 111 (46), 97 (81), 85 (64), 79 (84), 71 (63). Anal. Calcd for $C_9H_{14}S$: C, 70.07; H, 9.15. Found: C, 69.93; H, 9.24.

1-Methylthio-2-phenylethyne.[15] The title compound was prepared in 92% yield from phenylacetylene and dimethyldisulfide in the similar manner described above. ^1H NMR ($CDCl_3$): δ 2.46 (s, 3H), 7.3-7.4 (m, 3H), 7.4-7.5 (m, 2H).

1-Methylsulfonyl-1-dodecyne. "Oxone" (14 g, 23 mmol) was added to a stirring solution of 1-methylthio-1-dodecyne (2.1 g, 10 mmol) in MeOH (7 mL) and H_2O (3 mL) at 0 °C. The reaction mixture was warmed to 25 °C and stirred at 25 °C for 24 h. The reaction mixture was diluted with Et_2O (20 mL) and the white solid was removed by filtration with Hyflo-super Cel. The filtrate was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography on silica gel with ethyl acetate-hexane (1:5) as eluent gave 2.3 g (96%) of 1-methylsulfonyl-1-dodecyne. Bp 135-137 °C (bath temp, 0.24 Torr); IR (neat):

2922, 2852, 2200, 1735, 1466, 1376, 1152, 962, 769 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.89 (t, *J*=6.0 Hz, 3H), 1.2–1.5 (m, 14H), 1.5–1.7 (m, 2H), 2.41 (t, *J*=7.0 Hz, 2H), 3.19 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 13.9 18.5, 22.4, 26.7, 28.6, 28.7, 29.0, 29.1, 29.3, 31.6, 46.5, 77.1, 95.4. Anal. Calcd for $C_{13}H_{24}O_2S$: C, 63.89; H, 9.90. Found: C, 63.95; H, 9.94.

1–Phenylsulfonyl–1–dodecyne. The title compound was prepared in 96% yield from 1–phenylthio–1–dodecyne and "oxone" in the similar manner described above. Bp 165–167 °C (bath temp, 0.26 Torr); IR (neat): 2922, 2852, 2196, 1447, 1331, 1163, 1090, 726, 685 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.5 Hz, 3H), 1.2–1.5 (m, 14H), 1.4–1.6 (m, 2H), 2.36 (t, *J*=7.0 Hz, 2H), 7.5–7.8 (m, 3H), 8.0–8.1 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 13.9, 18.7, 22.5, 26.8, 28.5, 28.7, 29.0, 29.1, 29.3, 31.7, 78.0, 97.8, 126.9, 129.1, 133.8, 141.9. Anal. Calcd for $C_{18}H_{26}O_2S$: C, 70.54; H, 8.55. Found: C, 70.53; H, 8.47.

1–Cyclohexyl–2–methylsulfonylethyne. The title compound was prepared in 94 % yield from 1–cyclohexyl–2–methylthioethyne and "oxone" in the similar manner described above. Bp 105–107 °C (bath temp, 1.0 Torr); IR (neat): 2930, 2856, 2192, 1450, 1326, 1151, 979, 787, 768, 659 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.3–2.0 (m, 10H), 2.5–2.7 (m, 1H), 3.19 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 24.2, 25.1, 28.6, 30.6, 46.6, 77.0, 98.5. Anal. Calcd for $C_9H_{14}O_2S$: C, 58.03; H, 7.58. Found: C, 57.95; H, 7.68.

1–Methylsulfinyl–1–dodecyne. "Oxone" (7.4 g, 12 mmol) was added to a stirring solution of 1–methylthio–1–dodecyne (2.1 g, 10 mmol) in MeOH (7 mL) and H_2O (3 mL) at 0 °C. The reaction mixture was warmed to 25 °C and stirred at 25 °C for 15 min. The reaction mixture was diluted with Et_2O (20 mL) and the white solid was removed by filtration with Hyflo–Super Cel^R. The filtrate was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography on silica gel with ethyl acetate–hexane (1:5–1:1) as eluent gave

1.1 g (48%) of 1-methylsulfinyl-1-dodecyne. Bp 120-122 °C (bath temp, 0.20 Torr); IR (neat): 2922, 2852, 2180, 1466, 1073, 960 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H), 1.2-1.5 (m, 14H), 1.5-1.7 (m, 2H), 2.43 (t, *J*=7.0 Hz, 2H), 2.94 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 13.9, 19.5, 22.5, 27.5, 28.7, 28.9, 29.2, 29.3, 29.4, 31.7, 43.7, 78.7, 104.7. Anal. Calcd for $C_{13}H_{24}OS$: C, 68.36; H, 10.59. Found: C, 68.27; H, 10.71.

General Procedure for the Reduction of 1-Alkynyl Sulfides. In a 50-mL reaction flask was placed $TaCl_5$ (0.72 g, 2.0 mmol) under an argon atmosphere. To the salt was added at 25 °C benzene (5 mL) and DME (5 mL) successively. Zinc dust (0.20 g, 3.0 mmol) was added to the stirring pale yellow solution of $TaCl_5$ and the resulting mixture was stirred at 25 °C for 40 min, pyridine (0.08 mL, 1.0 mmol) was added to the mixture and the resulting mixture was stirred at 25 °C for 10 min. To the mixture was added at 25 °C a solution of a 1-alkynyl sulfide (1.0 mmol) in DME and benzene (1:1, 2 mL) and the whole mixture was stirred at 25 °C. Aqueous NaOH solution (15 %, 2 mL) was added and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The crude product was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel gave a 1-alkenyl sulfide.

(*Z*)-1-Methylthio-1-dodecene.[16] ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.2 Hz, 3H), 1.2-1.5 (m, 16H), 2.10 (dt, *J*=7.2, 7.0 Hz, 2H), 2.25 (d, *J*=0.8 Hz, 3H), 5.53 (ddt, *J*=0.8, 9.3, 7.2 Hz, 1H), 5.86 (dd, *J*=0.8, 9.3 Hz, 1H). The *E*/*Z* ratio was determined by capillary GLPC (140 °C, t_r=4.8 min (*Z*) and 5.3 min (*E*)).

(*Z*)-1-Phenylthio-1-dodecene.[17] ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H), 1.2-1.5 (m, 16H), 2.25 (dt, *J*=7.1, 7.0 Hz, 2H), 5.83 (dt, *J*=9.2, 7.1 Hz, 1H), 6.19 (d, *J*=9.2, 1H), 7.2-7.4 (m, 5H). The *E*/*Z* ratio was determined by ^1H NMR. **(*E*)-1-Phenylthio-1-dodecene.** ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H),

1.2–1.5 (m, 16H), 2.2–2.3 (m, 2H), 6.00 (dt, *J*=15.0, 7.1 Hz, 1H), 6.14 (d, *J*=15.0 Hz, 1H), 7.2–7.4 (m, 5H).

(*Z*)–1–Cyclohexyl–2–methylthioethene.[18] ^{1}H NMR ($CDCl_3$): δ 1.0–1.4 (m, 5H), 1.6–1.8 (m, 5H), 2.2–2.4 (m, 1H), 2.26 (s, 3H), 5.40 (dd, *J*=9.2, 9.4 Hz, 1H), 5.78 (d, 9.4 Hz, 1H). The *E*/*Z* ratio was determined by capillary GLPC (90 °C, t_r=5.0 min (*Z*) and 6.3 min (*E*)).

(*Z*)–1–Methylthio–2–phenylethene.[19] ^{1}H NMR ($CDCl_3$): δ 2.39 (s, 3H), 6.20 (d, *J*=10.9 Hz, 1H), 6.43 (d, *J*=10.9 Hz, 1H), 7.2–7.6 (m, 5H). The *E*/*Z* ratio was determined by capillary GLPC (90 °C, t_r=9.1 min (*Z*) and 10.0 min (*E*)).

General Procedure for the Reduction of 1–Alkynyl Sulfones. In a 50–mL reaction flask was placed $TaCl_5$ (1.1 g, 3.0 mmol) under an argon atmosphere. To the salt was added at 25 °C benzene (7.5 mL) and DME (7.5 mL) successively. Zinc dust (0.29 g, 4.5 mmol) was added to the stirring pale yellow solution of $TaCl_5$ and the resulting mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of an alkynyl sulfone (1.0 mmol) in DME and benzene (1:1, 2 mL) and the whole mixture was stirred at 25 °C. H_2O (3 mL) was added and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo–Super Cel and washed with ethyl acetate (3x5 mL). The crude product was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel gave a 1–alkenyl sulfone.

(*Z*)–1–Methylsulfonyl–1–dodecene. Bp 125–157 °C (bath temp, 0.14 Torr); IR (neat): 2922, 2852, 1625, 1465, 1307, 1135, 961, 786 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.5 Hz, 3H), 1.2–1.6 (m, 16H), 2.66 (dt, *J*=7.4, 7.1 Hz, 2H), 2.97 (s, 3H), 6.26 (d, *J*=11.2 Hz, 1H), 6.38 (dt, *J*=11.2, 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.5, 27.8, 28.7, 29.1, 29.2, 29.4, 29.5, 31.8, 43.7, 129.3, 148.5; MS *m*/*z* (rel intensity): 246 (M^+, 6), 167 (8), 166 (25), 120 (86), 97 (76), 96 (100), 83 (55), 82

(56). Anal. Calcd for $C_{13}H_{26}O_2S$: C, 63.37; H, 10.64. Found: C, 63.13; H, 10.86. The *E/Z* ratio was determined by ^1H NMR analysis.

(Z)-1-Phenylsulfonyl-1-dodecene.[20] ^1H NMR ($CDCl_3$): δ 0.89 (t, *J*=6.5 Hz, 3H), 1.2–1.5 (m, 16H), 2.6–2.8 (m, 2H), 6.25 (dt, *J*=11.1, 6.5 Hz, 1H), 6.31 (d, *J*=11.1 Hz, 1H), 7.5–7.9 (m, 3H), 7.9–8.0 (m, 2H). The *E/Z* ratio was determined by ^1H NMR analysis.

(Z)-1-Cyclohexyl-2-methylsulfonylethene. Mp 75 °C; Bp 107–109 °C (bath temp, 1 Torr); IR (nujol): 1628, 1448, 1321, 1138, 974, 613 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.0–1.5 (m, 5H). 1.6–1.9 (m, 5H); 2.97 (s, 3H), 3.2–3.4 (m, 1H), 6.16 (dd, *J*=11.2, 13.4 Hz, 1H), 6.20 (d, *J*=11.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 24.9, 25.5, 32.0, 36.5, 44.0, 127.4, 152.9; MS *m/z* (rel intensity): 188 (M^+, 63), 109 (55), 93 (82), 79 (100), 67 (99), 41(71). Anal. Calcd for $C_9H_{16}O_2S$: C, 57.41; H, 8.57. Found: C, 57.12; H, 8.74. The *E/Z* ratio was determined by ^1H NMR analysis.

Reaction with 1-Methylsulfinyl-1-dodecyne and $TaCl_5$-Zn system. In a 50-mL reaction flask was placed $TaCl_5$ (0.72 g, 2.0 mmol) under an argon atmosphere. To the salt was added at 25 °C benzene (5 mL) and DME (5 mL) successively. Zinc dust (0.20 g, 3.0 mmol) was added to the stirring solution of $TaCl_5$ and the resulting mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 1-methylsulfinyl-1-dodecyne (0.23 g, 1.0 mmol) in DME and benzene (1:1, 2 mL) and the whole mixture was stirred at 25 °C for 30 min. Aqueous NaOH solution (15 %, 2 mL) was added and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The crude product was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel gave 0.16 g (64%) of 1-chloro-1-methylthio-1-dodecene and 0.02 g (9%) of 1-methylthio-1-dodecene.

1-Chloro-1-methylthio-1-dodecene. One isomer: R_f=0.79 (hexane); bp

95–97 °C (bath temp. 0.23 Torr); IR (neat): 2922, 2852, 1730, 1465, 1275, 848 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H), 1.2–1.5 (m, 16H), 2.24 (dt, *J*=7.6, 7.2 Hz, 2H), 2.35 (s, 3H), 5.98 (t, *J*=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 16.7, 22.7, 28.9, 29.1, 29.2, 29.3, 29.4, 29.6, 30.5, 31.9, 128.1, 136.3; MS *m/z* (rel intensity): 250 (M^++2, 7), 248 (M^+, 19), 213 (40), 123 (36), 121 (100), 109 (26), 97 (9), 95 (40), 83 (18). Anal. Calcd for $C_{13}H_{25}SCl$: C, 62.74; H, 10.13. Found: C, 62.99; H, 10.37. The other isomer: R_f=0.71 (hexane); bp 95–97 °C (bath temp. 0.23 Torr); IR (neat): 2922, 2852, 1730, 1459, 1272 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.3 Hz, 3H), 1.2–1.5 (m, 16H), 2.21 (dt, *J*=7.1, 7.0 Hz, 2H), 2.35 (s, 3H), 5.97 (t, *J*=7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 17.2, 22.7, 28.3, 28.9, 29.2, 29.3, 29.4, 29.6, 29.9, 31.9, 128.6, 133.2; MS *m/z* (rel intensity): 250, (M^++2, 8), 248 (M^+, 14), 213 (35), 123 (37), 121 (100), 95 (37), 83 (18). Anal. Calcd for $C_{13}H_{25}ClS$: C, 62.74; H, 10.13. Found: C, 63.01; H, 10.42.

General Procedure for the Synthesis of Allylic Alcohols from 1-Alkynyl Sulfides and Carbonyl Compounds. To a stirring solution of $TaCl_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and Benzene (1:1, 10 mL) at 25 °C under an argon atmosphere was added zinc dust (0.20 g, 3.0 mmol), and the mixture was stirred at 25 °C for 40min. To the mixture was added at 25 °C a solution of a 1-alkynyl sulfide (1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C. After consumption of the alkynyl sulfide was confirmed by TLC, THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) was added successively to the mixture. After the reaction mixture was stirred at 25 °C for 20 min, carbonyl compound (2.0 mmol) was added to the mixture at 25 °C, and the resulting mixture was stirred at 25 °C for 30 min. Aqueous NaOH solution (15 %, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The crude product was dried over $MgSO_4$ and

concentrated *in vacuo*. Purification by column chromatography on silica gel gave the desired allylic alcohol.

(*E*)-2-Decyl-1-methylthio-5-phenyl-1-penten-3-ol. IR (neat): 3360, 2920, 2852, 1456, 1031, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.5 Hz, 3H), 1.2–1.5 (m, 17H), 1.87 (ddd, *J*=6.5, 7.9, 7.9 Hz, 2H), 2.0–2.2 (m, 2H), 2.27 (s, 3H), 2.63 (dt, *J*=14.3, 7.9 Hz, 1H), 2.75 (dt, *J*=14.3, 7.9 Hz, 1H), 4.0–4.1 (m, 1H), 5.94 (s, 1H), 7.2–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 17.1, 22.3, 28.3, 29.3, 29.5, 29.6, 30.0, 31.9, 32.1, 37.1, 75.2, 123.8, 125.8, 128.3, 128.4, 141.0, 141.8; MS *m/z* (rel intensity) of the corresponding trimethylsilyl ether: 420 (M^+, 18), 373 (62), 316 (24), 315 (100). HRMS *m/z* of the trimethylsilyl ether, calcd for $C_{25}H_{44}OSSi$ (M^+): 420.2884, found 420.2859.

(*E*)-2-Decyl-5-phenyl-1-phenylthio-1-penten-3-ol. IR (neat): 3424, 2922, 2852, 1740, 1584, 1456, 1025, 737, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.0 Hz, 3H), 1.2–1.5 (m, 15H), 1.5–1.6 (m, 2H), 1.9–2.0 (m, 2H), 2.1–2.4 (m, 2H), 2.6–2.9 (m, 2H), 4.2–4.3 (m, 1H), 6.28 (s, 1H), 7.2–7.5 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 14.2, 22.7, 28.9, 29.4, 29.6, 30.0, 31.9, 32.1, 37.3, 75.1, 119.9, 125.8, 125.9, 126.3, 128.3, 128.4, 128.7, 129.0, 141.7, 145.4; MS *m/z* (rel intensity) of the corresponding trimethylsilyl ether: 482 (M^+, 25), 379 (20), 377 (100), 301 (5), 68 (2). HRMS *m/z* of the trimethylsilyl ether ($C_{30}H_{46}OSSi$), calcd for $C_{27}H_{37}S$ (m^+–$OSiMe_3$): 393.2618, found 393.2617.

(*Z*)-1-Phenyl-4-phenylthio-4-pentadecen-3-ol. IR (neat): 3364, 2922, 2852, 1735, 1584, 1466, 1024, 737, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.87 (t, *J*=6.4 Hz, 3H), 1.2–1.5 (m, 16H), 1.8–2.1 (m, 3H), 2.3–2.4 (m, 2H), 2.5–2.8 (m, 2H), 4.1–4.2 (m, 1H), 6.31 (t, *J*=7.1 Hz, 1H), 7.1–7.4 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 28.9, 29.3, 29.4, 29.6, 29.7, 31.9, 37.8, 75.0, 125.8, 128.1, 128.3, 128.4, 128.9, 135.1, 135.9, 139.7, 141.8; MS *m/z* (rel intensity) of the corresponding trimethylsilyl ether: 482 (M^+, 26), 379 (22), 377 (100), 301 (5), 75 (1). HRMS *m/z*

of the trimethylsilyl ether ($C_{30}H_{46}OSSi$), calcd for $C_{27}H_{37}S$ (m^+–$OSiMe_3$): 393.2618, found 393,2647.

(*E*)–1–Cyclohexyl–2–decyl–3–methylthio–2–propen–1–ol. IR (neat): 3392, 2922, 2850, 1450, 1262, 1013, 809 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H), 0.9–1.1 (m, 2H), 1.1–1.6 (m, 23H), 1.6–1.9 (m, 2H), 1.9–2.0 (m, 1H), 2.0–2.2 (m, 2H), 2.27 (s, 3H), 3.7–3.8 (m, 1H), 5.86 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 17.2, 22.7, 26.0, 26.2, 26.4, 28.5, 29.3, 29.4, 29.6, 29.7, 30.0, 30.1, 31.9, 41.4, 81.0, 124.2, 140.3; MS *m/z* (rel intensity) of the corresponding trimethylsilyl ether: 398(M^+, 5), 317 (11), 316 (27), 315 (100). HRMS *m/z* of the trimethylsilyl ether, calcd for $C_{23}H_{46}OSSi$ (M^+): 398.3040, found 398.3012.

(*E*)–1–(1–Decyl–2–methylthioethenyl)cyclohexanol. IR (neat): 3428, 2920, 2854, 1447, 1255, 1129, 957, 808 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H), 1.2–1.6 (m, 17H), 1.5–1.8 (m, 10H), 2.1–2.2 (m, 2H), 2.28 (s, 3H), 6.04 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 17.2, 21.9, 22.6, 25.5, 28.9, 29.3, 29.6, 30.0, 30.3, 31.9, 36.2, 74.5, 121.9, 145.2; MS *m/z* (rel intensity) of the corresponding trimethylsilyl ether: 384 (M^+, 15), 369 (100), 337 (93), 279 (94), 73 (76). HRMS *m/z* of the trimethylsilyl ether, calcd for $C_{22}H_{44}OSSi$ (M^+): 384.2884, found 384,2868.

(*E*)–1–(1–Decyl–2–phenylthioethenyl)cyclohexanol. R_f=0.32 (ethyl acetate–hexane, 1:10); IR (neat): 3426, 2924, 2852, 1584, 1479, 1440, 737, 688 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.5 Hz, 3H), 1.2–1.5 (m, 17H), 1.5–1.8 (m, 10H), 2.2–2.4 (m, 2H), 6.38 (s, 1H), 7.2–7.5 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 21.9, 22.7, 25.5, 29.3, 29.6, 29.7, 30.0, 30.3, 31.9, 36.3, 74.9, 118.2, 126.0, 128.8, 128.9, 136.9, 149.7; MS *m/z* (rel intensity) of the corresponding trimethylsilyl ether: 446 (M^+, 55), 369 (22), 357 (11), 337 (100), 279 (14), 171 (1), 75 (1). HRMS *m/z* of the trimethylsilyl ether ($C_{27}H_{46}OSSi$), calcd for $C_{24}H_{36}S$ (m^+–Me_3SiOH): 356.2540, found 356.2565.

(*Z*)-1-(1-Phenylthio-1-dodecenyl)cyclohexanol. R_f=0.43 (ethyl acetate-hexane, 1:10); IR (neat): 3426, 2922, 2852, 1583, 1478, 1439, 736, 688 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.5 Hz, 3H), 1.2-1.4 (m, 16H), 1.5-1.8 (m, 8H), 1.9-2.0 (m, 1H), 2.22 (dt, *J*=6.9, 7.0 Hz, 2H), 2.4-2.6 (m, 2H), 6.43 (t, *J*=6.9 Hz, 1H), 7.1-7.3 (m, 1H), 7.2-7.3 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.0, 22.7, 25.5, 28.8, 29.3, 29.4, 29.5, 29.6, 29.7, 30.5, 31.9, 36.5, 74.9, 124.9, 126.3, 128.7, 137.4, 138.9, 139.5; MS *m/z* (rel intensity) of the corresponding trimethylsilyl ether: 446 (M^+, 25), 276 (35), 171 (100), 68 (11). HRMS *m/z* of the trimethylsilyl ether ($C_{27}H_{46}OSSi$), calcd for $C_{24}H_{37}S$ (m^+-Me_3SiO): 357.2618, found 357.2553.

(*E*)-2-Cyclohexyl-1-methylthio-5-phenyl-1-penten-3-ol. IR (neat): 3366, 2922, 2850, 1603, 1495, 1448, 1041, 746, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.2-1.5 (m, 4H), 1.4-1.6 (m, 5H), 1.6-2.0 (m, 4H), 2.2-2.5 (m, 1H), 2.27 (s, 3H), 2.63 (dt, *J*=8.1, 14.1 Hz, 1H), 2.79 (dt, *J*=8.1, 14.1 Hz, 1H), 4.1-4.2 (m, 1H), 5.95 (s, 1H), 7.2-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 17.7, 26.0, 26.7, 30.3, 32.4, 38.3, 40.7, 73.1, 123.2, 125.8, 128.3, 128.4, 142.0, 144.9; MS *m/z* (rel intensity) of the corresponding trimethylsilyl ether: 362 (M^+, 5), 315 (19), 259 (10), 257 (100), 91 (33), 73 (45). HRMS *m/z* of the trimethylsilyl ether, calcd for $C_{21}H_{34}OSSi$ (M^+): 362.2101, found 362.2098. .

(*E*)-1-(1-Cyclohexyl-2-methylthioethenyl)cyclohexanol. IR (neat): 3430, 2920, 2848, 1448, 1162, 957 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.1-1.4 (m, 6H), 1.4-1.9 (m, 13H), 2.0-2.2 (m, 3H), 2.27 (s, 3H), 6.02 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 18.5, 21.8, 25.4, 25.8, 27.0, 28.9, 35.1, 39.9, 75.4, 120.4, 147.9; MS *m/z* (rel intensity) of the corresponding trimethylsilyl ether: 326 (M^+, 31), 311 (100), 279 (99), 243 (38), 229 (51), 171 (42), 73 (78). HRMS *m/z* of the trimethylsilyl ether, calcd for $C_{18}H_{34}OSSi$ (M^+): 326.2101, found 326.2108.

(*E*)-2,5-Diphenyl-1-methylthio-1-penten-3-ol. IR (neat): 3360, 3022, 2918, 1603, 1492, 1440, 1030, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.7-1.9 (m, 3H),

2.26 (s, 3H), 2.64 (ddt, *J*=6.9, 6.9, 9.1 Hz, 1H), 2.75 (ddt, *J*=6.9, 6.9, 9.1 Hz, 1H), 4.4–4.5 (m, 1H), 6.29 (s, 1H), 7.1–7.5 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 17.5, 31.8, 37.5, 75.3, 125.7, 126.8, 127.5, 128.27, 128.33, 128.6, 137.6, 140.1, 141.7; MS *m/z* (rel intensity) of the corresponding trimethylsilyl ether: 356 (M^+, 8), 309 (35), 251 (100), 91 (40), 73 (63). HRMS *m/z* of the trimethylsilyl ether, calcd for $C_{21}H_{28}OSSi$ (M^+): 356.1631, found 356.1643.

(*E*)-1-(2-Methylthio-1-phenylethenyl)cyclohexanol. IR (neat): 3426, 2926, 2854, 1441, 1156, 974, 766, 700, 647 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.4–1.6 (m, 11H), 2.23 (s, 3H), 6.39 (s, 1H), 7.2–7.3 (m, 2H), 7.3–7.5 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 17.1, 21.9, 25.2, 36.5, 74.0, 125.6, 127.2, 128.2, 129.5, 138.7, 145.4; MS *m/z* (rel intensity) of the corresponding trimethylsilyl ether: 320 (M^+, 23), 305 (91), 273 (38), 215 (28), 171 (33), 115 (14), 73 (100), 45 (22). HRMS *m/z* of the trimethylsilyl ether, calcd for $C_{18}H_{28}OSSi$ (M^+): 320.1631, found 320.1656.

General Procedure for the Synthesis of Allylic Alcohols from 1-Alkynyl Sulfones and Carbonyl Compounds. To a stirring solution of $TaCl_5$ (1.1 g, 3.0 mmol) in a mixed solvent of DME and Benzene (1:1, 15 mL) at 25 °C under an argon atmosphere was added zinc dust (0.29 g, 4.5 mmol), and the mixture was stirred at 25 °C for 40min. To the mixture was added at 25 °C a solution of a 1-alkynyl sulfone (1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C. After consumption of the 1-alkynyl sulfide was confirmed by TLC, THF (8.5 mL) was added to the mixture. After the reaction mixture was stirred at 25 °C for 20 min, carbonyl compound (2.0 mmol) was added to the mixture at 25 °C, and the resulting mixture was stirred at 25 °C for 30 min. H_2O (3 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The crude product was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel gave

the desired allylic alcohol.

(*E*)-2-Decyl-1-methylsulfonyl-5-phenyl-1-penten-3-ol. R_f=0.22 (ethyl acetate-hexane, 2:1); bp 215-217 °C (bath temp, 0.30 Torr); IR (neat): 3468, 2924, 2852, 1629, 1457, 1300, 1131, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H), 1.2-1.4 (m, 14H), 1.4-1.6 (m, 2H), 1.7-1.9 (m, 2H), 1.9-2.2 (m, 2H), 2.6-3.0 (m, 3H), 2.95 (s, 3H), 4.2-4.3 (m, 1H), 6.49 (s, 1H), 7.2-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 28.8, 29.2, 29.3, 29.5, 30.0, 31.7, 31.8, 37.1, 44.0, 72.3, 123.5, 126.1, 128.4, 128.5, 141.0, 163.9. Anal. Calcd for $C_{22}H_{36}O_3S$: C, 69.43; H, 9.53. Found: C, 69.33; H, 9.79.

(*Z*)-4-Methylsulfonyl-1-phenyl-4-pentadecen-3-ol. R_f=0.39 (ethyl acetate-hexane, 2:1); bp 207-209 °C (bath temp, 0.20 Torr); IR (neat): 3480, 2924, 2852, 1636, 1455, 1298, 1127, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.3 Hz, 3H), 1.2-1.6 (m, 16H), 2.0-2.2 (m, 2H), 2.5-3.0 (m, 5H), 2.99 (s, 3H), 4.4-4.5 (m, 1H), 6.31 (t, *J*=7.8 Hz, 1H), 7.2-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 28.7, 29.0, 29.2, 29.3, 29.4, 29.5, 31.8, 32.2, 37.8, 45.0, 72.0, 126.0, 128.4, 128.5, 141.1, 142.5, 144.8. Anal. Calcd for $C_{22}H_{36}O_3S$: C, 69.43; H, 9.53. Found: C, 69.42; H, 9.80.

(*E*)-2-Decyl-1-phenylsulfonyl-5-phenyl-1-penten-3-ol. R_f=0.15 (ethyl acetate-hexane, 5:1); bp 234-236 °C (bath temp, 0.21 Torr); IR (neat): 3486, 2924, 2852, 1625, 1448, 1304, 1146, 698, 687 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.89 (t, *J*=6.5 Hz, 3H), 1.2-1.5 (m, 16H), 1.6-1.8 (m, 2H), 1.8-2.2 (m, 2H), 2.6-2.7 (m, 2H), 2.9-3.0 (m, 1H), 4.1-4.2 (m, 1H), 6.52 (s, 1H), 7.1-7.4 (m, 5H), 7.5-7.6 (m, 3H), 7.9-8.0 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 28.8, 29.2, 29.3, 29.4, 29.5, 29.6, 30.0, 31.6, 31.9, 37.1, 72.9, 124.9, 126.1, 127.1, 128.4, 128.5, 129.1, 133.1, 141.0, 142.2, 162.7. Anal. Calcd for $C_{27}H_{38}O_3S$: C, 73.26; H, 8.65.

(*Z*)-1-Phenyl-4-phenylsulfonyl-4-pentadecen-3-ol. R_f=0.24 (ethyl acetate-hexane, 5:1); bp 234-236 °C (bath temp, 0.21 Torr); IR (neat): 3488,

2922, 2852, 1736, 1637, 1447, 1304, 1145, 698, 688 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.5 Hz, 3H), 1.1–1.4 (m, 16H), 2.0–2.2 (m, 2H), 2.4–2.6 (m, 2H), 2.6–2.9 (m, 2H), 2.9–3.0 (m, 1H), 4.4–4.5 (m, 1H), 6.28 (t, *J*=7.7 Hz, 1H), 7.2–7.4 (m, 5H), 7.5–7.7 (m, 3H), 7.9–8.0 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.5, 28.4, 28.5, 29.0, 29.1, 29.3, 29.4, 31.7, 32.0, 38.0, 70.7, 125.7, 127.0, 128.2, 128.3, 128.9, 133.0, 141.0, 141.7, 143.1, 144.6. Anal. Calcd for $C_{27}H_{38}O_3S$: C, 73.26; H, 8.65. Found: C, 73.19; H, 8.78.

(*E*)-1-Cyclohexyl-2-decyl-3-methylsulfonyl-3-propen-1-ol. R_f=0.21 (ethyl acetate–hexane, 1:3); bp 190–192 °C (bath temp, 0.30 Torr); IR (neat): 3486, 2924, 2852, 1628, 1451, 1296, 1131, 733 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.5 Hz, 3H), 0.9–1.5 (m, 18H), 1.4–1.7 (m, 6H), 1.7–1.9 (m, 2H), 2.0–2.3 (m, 2H), 2.8–3.0 (m, 2H), 2.97 (s, 3H), 4.0–4.1 (m, 1H), 6.40 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 25.8, 26.0, 26.1, 26.4, 29.0, 29.2, 29.5, 29.7, 30.1, 30.5, 31.8, 41.2, 44.1, 77.7, 124.4, 162.5. Anal. Calcd for $C_{20}H_{38}O_3S$: C, 66.99; H, 10.68. Found: C, 66.85; H, 10.74.

(*Z*)-1-Cyclohexyl-2-methylsulfonyl-2-tridecen-1-ol. R_f=0.27 (ethyl acetate–hexane, 1:3); bp 190–192 °C (bath temp, 0.39 Torr); IR (neat): 3484, 2922, 2852, 1631, 1450, 1302, 1128, 730 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.5 Hz, 3H), 1.0–1.5 (m, 20H), 1.5–1.9 (m, 6H), 2.0–2.1 (m, 1H), 2.5–2.7 (m, 2H), 2.9–3.1 (m, 1H), 3.01 (s, 3H), 4.00 (d, *J*=8.6 Hz, 1H), 6.23 (t, *J*=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 25.7, 25.9, 26.2, 28.8, 28.9, 29.0, 29.1, 29.5, 30.3, 31.8, 42.2, 45.2, 79.4, 141.1, 146.0. Anal. Calcd for $C_{20}H_{38}O_3S$: C, 66.99; H, 10.68. Found: C, 66.73; H, 10.71.

(*E*)-1-(1-Decyl-2-methylsulfonylethenyl)cyclohexanol. R_f=0.32 (ethyl acetate–hexane,1:2); bp 189–191 °C (bath temp, 0.20 Torr); IR (neat): 3478, 2924, 2852, 1617, 1467, 1294, 1132, 964, 732 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.4 Hz, 3H), 1.1–1.5 (m, 14H), 1.4–1.8(m, 13H), 2.5–2.6 (m, 2H), 2.96 (s, 3H), 6.58

(s, 1H); ^{13}C NMR ($CDCl_3$): δ 13.9, 21.2, 22.5, 24.9, 28.2, 29.1, 29.2, 29.5, 30.4, 31.3, 31.7, 35.0, 43.9, 75.3, 122.9, 167.3. Anal. Calcd for $C_{19}H_{36}O_3S$: C, 66.23; H, 10.53. Found: C, 66.14; H, 10.81.

(*E*)-2-Cyclohexyl-1-methylsulfonyl-5-phenyl-1-penten-3-ol. R_f=0.07 (ethyl acetate-hexane, 1:3); bp 195-197 °C (bath temp, 0.29 Torr); IR (neat): 3468, 2924, 2852, 1453, 1289, 1132, 732, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.0-1.5 (m, 5H), 1.5-1.9 (m, 6H), 1.8-2.1 (m, 2H), 2.6-3.0 (m, 2H), 2.88 (s, 3H), 3.3-3.5 (m, 1H), 4.3-4.4 (m, 1H), 6.45 (s, 1H), 7.2-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 25.6, 26.0, 30.7, 30.9, 32.2, 39.3, 44.3, 69.5, 124.7, 126.1, 128.5, 128.6, 141.1, 168.0. Anal. Calcd for $C_{18}H_{26}O_3S$: C, 67.04; H, 8.13. Found: C, 67.32; H, 8.11.

(*Z*)-1-Cyclohexyl-2-methylsulfonyl-5-phenyl-1-penten-3-ol. R_f=0.18 (ethyl acetate-hexane, 1:3); bp 195-197 °C (bath temp, 0.29 Torr); IR (neat): 3478, 2924, 2850, 1451, 1286, 1129, 748, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.0-1.5 (m, 5H), 1.6-1.9 (m, 6H), 2.0-2.2 (m, 2H), 2.6-3.0 (m, 2H), 3.00 (s, 3H), 3.0-3.2 (m, 1H), 4.4-4.5 (m, 1H), 6.07 (d, *J*=11.1 Hz, 1H), 7.2-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 25.0, 25.5, 32.1, 32.2, 37.6, 37.8, 45.6, 72.0, 126.0, 128.4, 128.5, 140.5, 141.1, 149.2. Anal. calcd for $C_{18}H_{26}O_3S$: C, 67.04; H, 8.13. Found: C, 67.17; H, 8.17.

Typical Procedure for Preparation of α,β-Unsaturated Aldehyde by Acid Hydrolysis of Oxatantalacyclopentene Complex. To a stirring solution of $TaCl_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and benzene (1:1, 10 mL) at 25 °C under an argon atmosphere was added zinc dust (0.20 g, 3.0 mmol), and the mixture was stirred at 25 °C for 40min. To the mixture was added at 25 °C a solution of 1-methylthio-1-dodecyne (0.21 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C. After consumption of the alkynyl sulfide was confirmed by TLC, THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) was added successively to the mixture. After the reaction mixture was

stirred at 25 °C for 20 min, 3-phenylpropanal (0.26 g, 2.0 mmol) was added to the mixture at 25 °C, and the resulting mixture was stirred at 25 °C for 30 min. H_2O (5 mL) and $TiCl_4$ (2.0 mL of 1.0 M CH_2Cl_2 solution, 2.0 mmol) were added successively to the mixture. After the reaction mixture was stirred at 25 °C for 1 h, and aqueous NaOH solution (15 %, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The crude product was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel with ethyl acetate-hexane (1:20) as eluent gave 0.21 g (70%) of (*E*)-2-decyl-5-phenyl-2-pentenal.

(*E*)-2-Decyl-5-phenyl-2-pentenal. R_f=0.30 (ethyl acetate-hexane, 1:10); bp 156-158 °C (bath temp, 0.22 Torr); IR (neat): 2922, 2852, 1688, 1640, 1455, 746, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.87 (t, *J*=6.3 Hz, 3H), 1.2-1.4 (m, 16H), 2.1-2.2 (m, 2H), 2.6-2.8 (m, 2H), 2.8-2.9 (m, 2H), 6.45 (t, *J*=7.1 Hz, 1H), 7.2-7.5 (m, 5H), 9.35 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 24.0, 28.6, 29.3, 29.4, 29.5, 29.6, 30.6, 31.8, 34.7, 126.3, 128.3, 128.5, 140.5, 144.3, 153.2, 195.0; MS *m/z* (rel intensity): 300 (M^+, 24), 159 (47), 117 (19), 104 (24), 91 (100). Anal. Calcd for $C_{21}H_{32}O$: C, 83.94; H, 10.73. Found: C, 84.10; H, 10.80.

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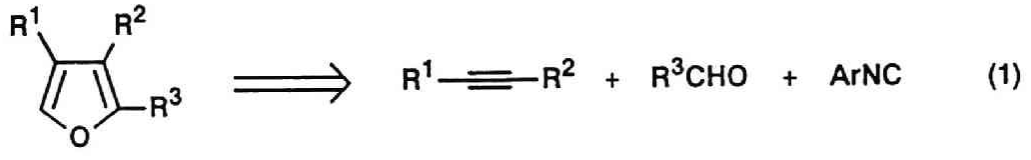
CHAPTER 7

Regioselective Synthesis of Highly Substituted Furans *via* Tantalum–Alkyne Complexes.

A variety of 2,3,4–trisubstituted furans are prepared by treatment of tantalum–alkyne complexes with aldehydes followed by addition of an isocyanide in DME–PhH–THF (1:1:1). The reaction also took place with carbon monoxide (ca. 1.2 atom), but the yield of the furan was only 13%. The regioselectivity of the reaction depends on the bulkiness of substituents on acetylenes and the bulkier substituents tend to possess 4–position of the produced furans. 4–Trialkylsilyl–substituted furans are produced exclusively when trialkylsilylacetylenes are employed.

Furan skeletons[1] are observed in many naturally occurring compounds[2] and moreover, they are important compounds as synthetic intermediates[1,3] such as diene components of the Diels–Alder reaction and latent 1,4–diketone moieties. Because regioselective introduction of carbon substituents into a simple furan is rather difficult,[4] they are sometimes prepared from acyclic precursors.[5] We disclose here a regioselective preparation of highly substituted furans from three components, i.e. acetylenes, aldehydes, and an isocyanide by means of low–valent tantalum (eq. 1).

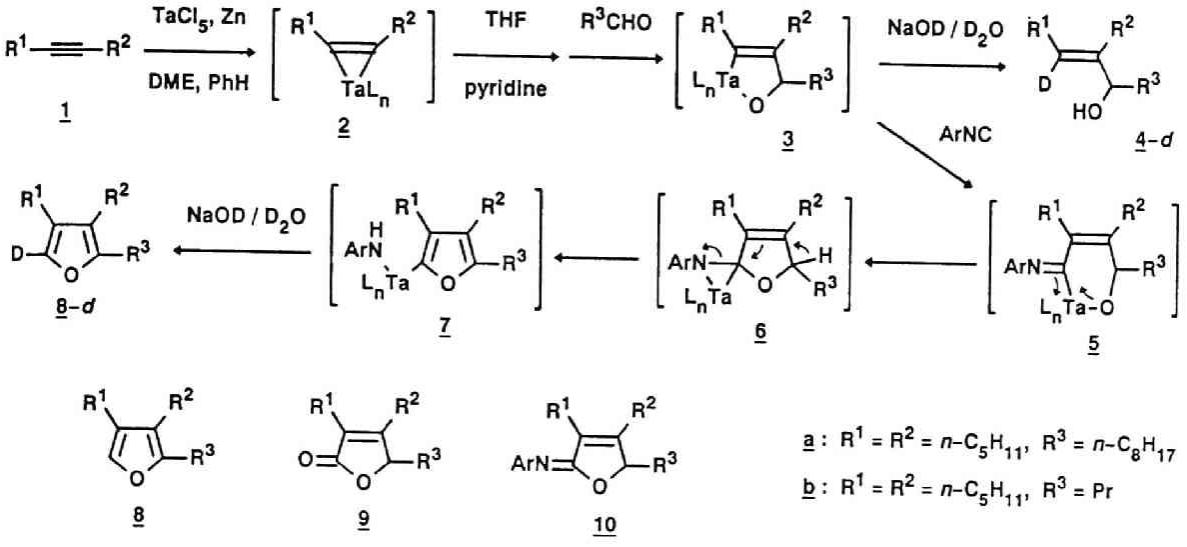


(1)

Insertion of carbon monoxide[6] or isocyanide[7] into metal–carbon bonds is a typical method for introducing one carbon unit into organometallic compounds. Although the insertion of isocyanide into tantalum–carbon bonds was first recognized in 1974,[8] the process has not been utilized in organic synthesis. Recently, we found a general and simple method for the preparation of tantalum–alkyne complexes[9,10] derived from low–valent tantalum and acetylenes. These complexes add to carbonyl compounds in a stereoselective manner to yield (E)–allylic alcohols.[9c] In this reaction, oxatantalacyclopentene **3** was postulated as an intermediate, because quenching the reaction mixture of **3a** (R^1=R^2=*n*–C_5H_{11}, R^3=*n*–C_8H_{17}) with alkaline D_2O furnished 3–deuterated allylic alcohol **4a–*d*** in 86% yield (94% deuterated). Thus we tried to examine the insertion of ArNC into the tantalum–carbon bond of the complex **3** (Scheme 1).

Reactive tantalacyclopropene **2a** (R^1=R^2=*n*–C_5H_{11}) was generated by the reaction between 6–dodecyne (1.0 equiv) and the low–valent tantalum derived from $TaCl_5$ (2.0 equiv) and zinc (3.0 equiv) in a mixed solvent of DME and benzene at 25 °C. Successive addition of THF, pyridine, and nonanal (1.2 equiv) to

Scheme 1



the reaction mixture gave oxatantalacyclopentene **3a** (not isolated).[9c] Treatment of **3a** with 2,6-dimethylphenyl isocyanide (1.0 equiv) at 25 °C for 20 min afforded furan **8a** in 66% yield.[9d] Neither butenolide[11] **9a** nor imino lactone[12] **10a** was formed.[13]

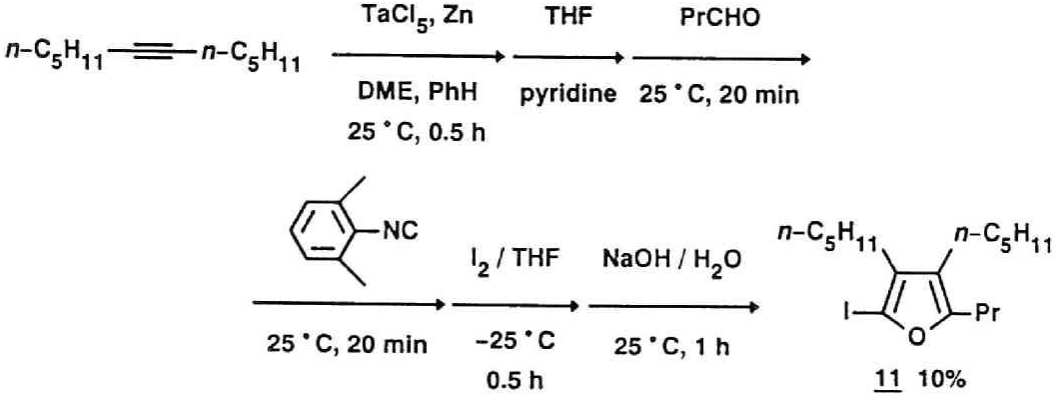
Yields of furans were critically dependent on the amounts of the isocyanide and the charge of excess isocyanide retarded the formation of furans.[14] For example, treatment of **3a** with 2.0 equiv of the isocyanide gave **8a** in 40% yield along with unreacted allylic alcohol **4a** in 15% yield. Decomposition of the furan **8a** took place gradually in the reaction mixture. Yield of the furan **8a** in the reaction between **3a** and 1.2 equiv of the isocyanide monitored by GLPC are as follows: 66% yield, 20 min; 55% yield, 1h; 31% yield, 14h. The reaction also took place with either cyanotrimethylsilane or carbon monoxide (ca. 1.2 atom), but the desired furan **8a** was obtained in only 29% and 13% yields, respectively.

The reaction proceeded under mild conditions and 2,3,4-trisubstituted furans were produced (Table 1). The yield of the furan was rather low when aliphatic isocyanide was used (run 3). The regioselectivities of the reactions are determined

at the insertion step of aldehydes into tantalacyclopropene **2** and are controlled by bulkiness of the substituents of the acetylenes.[9c] (Trialkylsilyl)acetylenes gave one of the regioisomers under high stereocontrol (runs 7 and 9). Because the formation of tantalum–alkyne complexes having bulky substituents was slow, 4 equiv of low-valent tantalum and 2 equiv of isocyanide were employed (runs 6, 7, and 9). Regiochemistry of the furan derived from a tantalum–1–dodecyne complex was confirmed by ^{1}H NMR analysis (run 1).[15] Trialkylsilyl–substituted furans were desilylated with a $(HF)_x$–pyridine complex [5h] and the regiochemistries were ascertained by comparison with the authentic compounds obtained from the corresponding terminal alkynes.

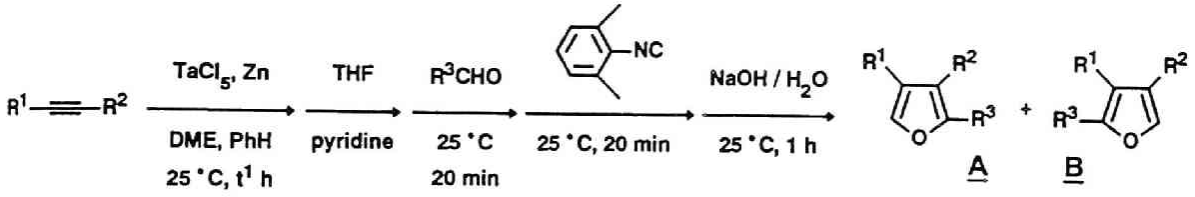
Plausible mechanisms for the reaction are outlined in Scheme 1. Insertion of an isocyanide into the carbon–tantalum bond of **3** would produce a tantalacycle **5**.[8,10d] Migration of oxygen from tantalum to the imino carbon would give a η^2–acylimidoyl complex **6**,[16] which would produce 2–furyltantalum **7** *via* oxygen–assisted elimination of NAr. The affinity of tantalum for heteroatoms and the high strain of azatantalacyclopropane in the η^2–acylimidoyl complex **6** are the driving force for this migration process. The presence of the 2–furyltantalum **7** was ascertained by the fact that quenching of the reaction mixture of **7b** with alkaline D_2O afforded 2–deuterated furan **8b–*d*** (R^1=R^2=*n*–C_5H_{11}, R^3=*n*–C_3H_7, 47% yield, 91% deuterated).

Although the postulated 2–furyltantalum could not be trapped completely, quenching with iodine at –25 °C produced 2–iodofuran **11** in 10% yield (eq 2).



11 10%

Table 1. Synthesis of Furans from Alkynes, Aldehydes, and Isocyanides.[a]



Run	R^1	R^2	R^3	Ar	t^1 / h	Yield / %[b]	A / B[c]
1	n-$C_{10}H_{21}$	H	n-C_3H_7	2,6-$Me_2(C_6H_3)$	0.5	8[d]	>99 / <1
2	n-C_5H_{11}	n-C_5H_{11}	n-C_8H_{17}		0.5	66	--
3				[$Me_3CCH_2CMe_2NC$]	0.5	28	--
4				[Me_3SiCN]	0.5	29[e]	--
5	c-C_6H_{11}	n-C_6H_{13}	n-C_5H_{11}	2,6-$Me_2(C_6H_3)$	2	55	69 / 31
6	t-Bu	n-C_7H_{15}	n-C_3H_7		5	40[f]	98 / 2
7	Me_3Si	n-$C_{10}H_{21}$			2	57	94 / 6[g]
8		Ph			3.5	42[f]	>99 / <1[g]
9	t-$BuMe_2Si$	n-$C_{10}H_{21}$			3.5	54[f,h]	>99 / <1[g]

a) Reactions were carried out on a 1 mmol scale. Conditions: 2.0 equiv of $TaCl_5$, 3.0 equiv of zinc, 4.0 equiv of pyridine, 1.2 equiv of aldehyde, 1.0 equiv of isonitrile, DME-PhH-THF (1:1:1), 25 °C. b) Isolated yields. c) Reference 17. d) Polymer of 1-dodecyne was produced in the reaction of 1-dodecyne with the low-valent tantalum, and remained until workup. Half equiv of the isonitrile was used. e) Reaction was conducted without pyridine. f) Conditions: 4.0 equiv of $TaCl_5$, 6.0 equiv of zinc, 8.0 equiv of pyridine, 2.0 equiv of isonitrile. g) Reference 5h. h) The reaction mixture was stirred at 25 °C for 40 min after addition of the isonitrile.

Experimental Section

Preparation of Isocyanide. 2,6-dimethylphenyl isocyanide was prepared according to the standard procedure described in ref 18 and 1,1,3,3-tetramethylbuthyl isocyanide and trimethylsilyl isocyanide are commercially available

General Procedure for the Synthesis of Furans. In a 50-mL reaction flask was placed $TaCl_5$ (0.72 g, 2.0 mmol) under an argon atmosphere. To the salt were added at 25 °C benzene (5 mL) and DME (5mL) successively. Zinc dust (0.20 g, 3.0 mmol) was added to stirring a pale yellow solution of $TaCl_5$ in DME and benzene, and the resulting mixture was stirred at 25 °C for 40 min. The color of the mixture turned to greenish dark blue with a slightly exothermic process. To the mixture was added at 25 °C a solution of an alkyne (1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C. After consumption of the alkyne was confirmed by TLC, THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the reaction mixture was stirred at 25 °C for 15 min, carbonyl compound (1.2 mmol) was added, and the resulting mixture was stirred at 25 °C for 20 min. To this mixture was added 2,6-dimethylphenyl isocyanide (0.13 g, 1.0 mmol) at 25 °C, and the reaction mixture was stirred at 25 °C for an additional 20 min. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-super Cel and washed well with ethyl acetate (3x5 mL). Organic extracts were concentrated *in vacuo*, diluted with hexane, dried over $MgSO_4$ and concentrated *in vacuo* again. Purification by column chromatography on silica gel using hexane as an eluent gave furan.

4-Decyl-2-propylfuran. Bp 55-57 °C (bath temp, 0.10 Torr); IR (neat):

2954, 2922, 2852, 1546, 1466, 1459, 1123, 940, 797, 738, 721 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.2–1.8 (m, 18H), 2.31 (t, *J*=7.0 Hz, 2H), 2.54 (t, *J*=7.3 Hz, 2H), 5.87 (d, *J*=0.7 Hz, 1H), 7.06 (d, *J*=0.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 13.8, 14.1, 21.3, 22.7, 25.0, 29.4, 29.5, 29.6, 30.0, 30.2, 31.9, 106.4, 126.0, 136.6, 156.3; MS *m/z* (rel intensity): 250 (M^+, 8), 137 (22), 124 (100), 67 (12). Anal. Calcd for $C_{17}H_{30}O$: C, 81.54; H, 12.08. Found: C, 81.64; H, 12.20. The regiochemistry was confirmed by ^1H MNR analysis.[15]

2-Octyl-3,4-dipentylfuran (8a). Bp 69–67 °C (bath temp, 0.15 Torr); IR (neat): 2954, 2924, 2854, 1730, 1561, 1466, 1378, 1274, 1135, 1073, 738 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.1 (m, 9H), 1.2–1.7 (m, 24H), 2.2–2.3 (m, 4H), 2.51 (t, *J*=7.3 Hz, 2H), 7.02 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.8, 23.3, 23.4, 24.2, 24.7, 27.1, 29.4, 29.8, 30.0, 30.1, 31.2, 32.5, 32.6, 119.4, 126.5, 136.7, 152.3; MS *m/z* (rel intensity): 320 (M^+, 100), 264 (61), 179 (64), 151 (84), 109 (47). Anal. Calcd for $C_{22}H_{40}O$: C, 82.43; H, 12.58. Found C, 82.70; H, 12.81.

4-Cyclohexyl-3-hexyl-2-pentylfuran (A) and 3-Cyclohexyl-4-hexyl-2-pentylfuran (B). The regioisomer ratio was determined by capillary GLPC analysis (column temp 150 °C, t_r=29.5 min (**A**) and 30.5 min (**B**)) (**A**/**B**=69/31). Bp 90–92 °C (bath temp, 0.10 Torr); IR (neat, mixture of **A**/**B**=69/31): 2952, 2924, 2852, 1459, 1449, 1379, 1261, 1142, 889, 739 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.2–2.0 (m, 24H), 2.2–2.3 (m, 3H), 2.4–2.6 (m, 2H), 6.977 (s, 1H(**B**)), 6.984 (s, 1H(**A**)); ^{13}C NMR ($CDCl_3$): δ 14.0, 14.1, 22.5, 22.7, 23.6, 24.7, 26.3, 26.4, 26.9, 27.3, 28.4, 28.8, 29.3, 29.4, 29.45, 29.50, 31.1, 31.6, 31.65, 31.70, 31.8, 33.1, 34.3, 35.5, 118.1 (**A**), 123.2 (**B**), 125.5 (**B**), 131.8 (**A**), 135.1 (**A**), 136.1 (**B**), 151.1 (**B**), 151.5 (**A**); MS *m/z* (rel intensity): 304 (M^+, 54), 247 (48), 234 (53), 191 (100), 177 (35), 109 (54), 81 (43). Anal. Calcd for $C_{21}H_{36}O$: C, 82.83; H, 11.92. Found: C, 82.99; H, 12.22.

4-*tert*-Butyl-3-heptyl-2-propylfuran. $TaCl_5$ (4.0 equiv), zinc (6.0 equiv),

and pyridine (8.0 equiv) were employed and the regiochemistry ratio was determined by ^{1}H NMR analysis. Bp 80–82 °C (bath temp, 0.60 Torr); IR (neat): 2956, 2926, 2860, 1466, 1389, 1379, 1362, 1205, 1147, 1133, 1096, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.26 (s, 9H), 1.2–1.7 (m, 12H), 2.4–2.5 (m, 4H), 6.97 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 14.1, 21.8, 22.7, 24.8, 28.5, 29.1, 29.2, 30.2, 30.7, 31.4, 31.9, 118.5, 134.4, 134.7, 153.0; MS *m/z* (rel intensity): 264 (M^+, 23), 179 (48), 165 (27), 151 (46), 138 (49), 91 (22), 57 (100). Anal. Calcd for $C_{18}H_{32}O$: C, 81.75; H, 12.20. Found: C, 81.83; H, 12.36.

3-Decyl-4-(trimethylsilyl)-2-propylfuran (A) and 4-Decyl-3-(trimethylsilyl)-2-propylfuran (B). The regioisomer ratio was determined by capillary GLPC analysis (190 °C, t_r=4.5 min (**A**) and t_r=5.4 min (**B**) (**A**/**B**=94/6). Bp 100–102 °C (bath temp, 0.40 Torr); IR (neat, mixture of **A**/**B**=94/6): 2954, 2924, 2852, 1506, 1465, 1458, 1249, 1139, 1123, 837, 753, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 9H(**A**)), 0.24 (s, 9H(**B**)), 0.8–1.0 (m, 6H), 1.2–1.7 (m, 18H), 2.3–2.4 (m, 2H), 2.4–2.5 (m, 2H), 7.09 (s, 1H(**B**)), 7.11 (s, 1H(**A**)); ^{13}C NMR ($CDCl_3$): δ –0.14, 14.0, 14.1, 22.0, 22.7, 25.6, 28.0, 29.4, 29.5, 29.6, 29.8, 31.8, 31.9, 111.8 (**B**), 119.5 (**A**), 122.7 (**A**) 130.3 (**B**), 136.8 (**B**), 145.5 (**A**), 152.3 (**A**), 161.7 (**B**); MS *m/z* (rel intensity): 322 (M^+, 10), 195 (22), 167 (15), 154 (23), 75 (30), 73 (100). Anal. Calcd for $C_{20}H_{38}OSi$: C, 74.46; H, 11.87. Found: C, 74.20; H, 12.16. The sample was desilylated with $(HF)_x$–Py^{5h} and its regiochemistry was ascertained by comparison with the product from 1-dodecyne.

4-(Trimethylsilyl)-3-Phenyl-2-propylfuran. Bp 55–57 °C (bath temp, 0.15 Torr); IR (neat): 2956, 2898, 2870, 1508, 1249, 1164, 1120, 978, 838, 768, 754, 700, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.02 (s, 9H), 0.87 (t, *J*=7.3 Hz, 3H), 1.5–1.7 (m, 2H), 2.51 (t, *J*=7.3 Hz, 2H), 7.2–7.4 (m, 6H); ^{13}C NMR ($CDCl_3$): δ –0.31, 13.8, 22.0, 28.0, 120.4, 125.4, 126.7, 127.9, 130.0, 135.7, 145.6, 152.9; MS *m/z* (rel intensity): 258 (M^+, 36), 243 (32), 229 (34), 75 (40), 73 (100). Anal. Calcd for

$C_{16}H_{22}OSi$: C, 74.36; H, 8.58. Found: C, 74.20; H, 8.45. The sample was desilylated with $(HF)_x$–Py^{5h} and its regiochemistry was ascertained by comparison with the product from phenylacetylene.

4–(*tert*–Butyldimethylsilyl)–3–decyl–2–propylfuran. $TaCl_5$ (4.0 equiv), zinc (6.0 equiv), and pyridine (8.0 equiv) were employed. Bp 75–77 °C (bath temp, 0.30 Torr); IR (neat); 2952, 2924, 2852, 1501, 1465, 1249, 1141, 1126, 832, 821, 807, 769, 672 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.18 (s, 6H), 0.87 (s, 9H), 0.8–1.0 (m, 6H), 1.2–1.7 (m, 18H), 2.3–2.4 (m, 2H), 2.51 (t, *J*=7.3 Hz, 2H), 7.12 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 14.2, 17.0, 22.0, 22.8, 26.1, 26.8, 28.2, 29.4, 29.6, 29.7, 30.0, 32.0, 32.2, 116.5, 123.0, 146.3, 152.1; MS *m/z* (rel intensity): 364 (M^+, 9), 308 (26), 307 (100), 181 (57), 75 (35), 73 (33). Anal. Calcd for $C_{23}H_{44}OSi$: C, 75.75; H, 12.16. Found: C, 75.96; H, 12.33. The sample was desilylated with $(HF)_x$–Py^{5h} and its regiochemistry was ascertained by comparison with the product from 1–dodecyne.

3,4–Dipentyl–2–iodo–5–propylfuran (11). To a stirring solution of $TaCl_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and benzene (1:1, 10 mL) at 25 °C under an argon atmosphere was added zinc (0.20 g, 3.0 mmol), and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 6–dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C for 30 min. THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the reaction mixture was stirred at 25 °C for 15 min, butanal (0.086 g, 1.2 mmol) was added to the mixture, and the resulting mixture was stirred at 25 °C for an additional 20 min. To this mixture was added 2,6–dimethylphenyl isocyanide (0.13 g, 1.0 mmol) at 25 °C, and the reaction mixture was stirred at 25 °C for an additional 20 min. To the mixture was added at –25 °C a solution of I_2 (1.3g, 5.0 mmol) in THF (6 mL), and the whole mixture was stirred at –25 °C for 30 min. Aqueous NaOH solution

(15%, 2 mL) was added at −25 °C, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was filtered off with Hyflo-Super Cel, and washed well with ethyl acetate (3x5 mL). The organic extracts were washed with saturated $NaHSO_3$ (10 mL) and brine (10 mL). Organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the crude product by column chromatography on silica gel with hexane gave 0.038 g (10%) of 3,4-dipentyl-2-iodo-5-propylfuran. Bp 90-92 °C (bath temp, 0.30 Torr); IR (neat): 2954, 2928, 2856, 1625, 1459, 1378, 1168, 1133, 1094, 1002 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8-1.0 (m, 9H), 1.2-1.8 (m, 14H), 2.24 (t, *J*=8.7 Hz, 2H), 2.27 (t, *J*=9.2 Hz, 2H), 2.51 (t, *J*=7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 13.8, 14.0, 22.0, 22.5, 23.8, 25.5, 28.6, 29.5, 30.5, 31.7, 85.4, 121.0, 131.7, 157.2; MS *m/z* (rel intensity): 376 (M^+, 98), 347 (19), 249 (100), 193 (35). HRMS *m/z*, calcd for $C_{17}H_{29}OI$ (M^+): 376.1256, found 376.1250.

Typical Procedure for Protodesilylation. A mixture of 3-Decyl-4-(trimethylsilyl)-2-propylfuran and 4-decyl-2-propyl-3-(trimethylsilyl)furan (0.16 g, 0.5 mmol, a 94/6 mixture) in THF (3 mL) was placed in a Teflon beaker. Pyridine poly(hydrogenfluoride) (1.5 mL, 68% HF) was added in one portion, and the resulting mixture was allowed to stir at 25 °C for 1 h. The reaction mixture was carefully added to a stirred, ice-cooled mixture of hexane (20 mL) and saturated $NaHCO_3$ solution (20 mL) (Evolution of CO_2). After 5 min, solid $NaHCO_3$ was added in portions until the aqueous phase became saturated. The organic layer was then separated, and the aqueous layer was extracted with hexane (2x20 mL). The combined organic extracts were washed twice with water and brine. The crude product was dried ($MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography on silica gel afforded a mixture of 3-decyl-2-propylfuran and 4-decyl-2-propylfuran in 88% combined yield (0.11 g, 0.44 mmol, 94/6).

3-Decyl-2-propylfuran. Bp 55-57 °C (bath temp, 0.10 Torr); IR (neat):

2956, 2924, 2852, 1734, 1654, 1509, 1459, 1145, 722 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.2–1.7 (m, 18H), 2.31 (t, *J*=7.0 Hz, 2H), 2.52 (t, *J*=7.3 Hz, 2H), 6.19 (d, *J*=1.7 Hz, 1H), 7.22 (d, *J*=1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 13.8, 14.2, 22.0, 22.7, 24.7, 28.0, 29.4, 29.5, 29.7, 30.7, 32.0, 111.3, 119.0, 140.0, 151.0; MS *m/z* (rel intensity): 250 (M^+, 13), 223 (15), 137 (20), 124 (58), 123 (45), 95 (100), 82 (59). Anal. Calcd for $C_{17}H_{30}O$: C, 81.54; H, 12.08. Found: C, 81.84; H, 12.32.

3–Phenyl–2–propylfuran. Bp 50–52 °C (bath temp, 0.10 Torr); IR (neat): 2958, 2928, 2870, 1518, 1459, 1147, 1132, 960, 764, 732, 696, 680 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.95 (t, *J*=7.3 Hz, 3H), 1.7–1.8 (m, 2H), 2.75 (t, *J*=7.3 Hz, 2H), 6.49 (d, *J*=1.7 Hz, 1H), 7.2–7.4 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 13.9, 21.8, 28.9, 111.2, 120.9, 126.3, 127.8, 128.5, 134.3, 140.4, 151.8; MS *m/z* (rel intensity): 186 (M^+, 34), 157 (74), 129 (32), 128 (31), 58 (100). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.91; H, 7.35.

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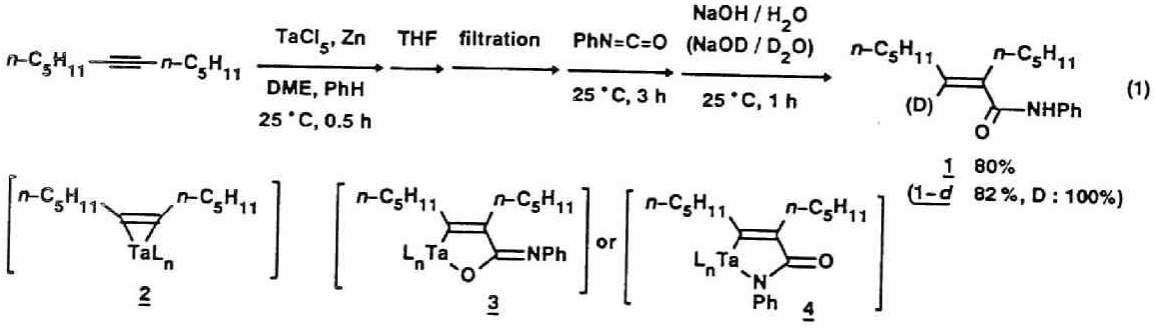
CHAPTER 8

Preparation of (*E*)-α,β-Unsaturated Amides from Tantalum-Alkyne Complexes and Isocyanates. Stereoselective Functionalization of Carbon-Carbon Triple Bonds.

Treatment of alkynes with low-valent tantalum derived from $TaCl_5$ and zinc produces tantalum-alkyne complexes (not isolated), which react *in situ* with phenyl isocyanate (or butyl isocyanate) to give (*E*)-α,β-unsaturated amides stereoselectively.

Insertion of unsaturated compounds into metal–carbon bonds is especially important as key steps of metal-mediated carbon–carbon bond formations.[1-4] Isocyanates are employed frequently as unsaturated compounds for introducing amide functionality at the metal-attached carbon.[5] We recently reported facile preparation of tantalum–alkyne complexes and utilized the complexes for the synthesis of (*E*)–allylic alcohols *via* insertion of carbonyl groups into tantalum–carbon bond.[4c] To explore the applicability of the tantalum–alkyne complexes, we chose isocyanates for stereoselective formation of α,β–unsaturated amides from alkynes.[1f,2b,6b]

Treatment of a tantalum–6–dodecyne complex **2**, derived from 6–dodecyne and a $TaCl_5$–Zn system,[4a] with phenyl isocyanate in a mixed solvent of DME–benzene–THF (1:1:1) at 25 °C gave a complex mixture; only 9% yield of the desired (*E*)–*N*–phenyl–2–pentyl–2–octenamide **1** could be obtained after workup. However, filtration of the reaction mixture containing tantalum–alkyne complexes under an argon atmosphere before addition of isocyanates improved the reaction markedly and **1** was produced in 80% yield. Deuterated amide **1**–***d*** was obtained in 82% yield (100% deuterated) by quenching the reaction mixture of **3** (or **4**) with alkaline D_2O.



(1)

The results of the reactions between tantalum–alkyne complexes and isocyanates are summarized in Table 1. Reactions between the tantalum–alkyne complexes and butyl isocyanate took place at 25 °C and *N*–butyl–2–alkenamides were produced in good to excellent yields. In contrast, *tert*–butyl– and trimethylsilyl isocyanates were almost unreactive due to the bulkiness of the substituents (runs 3 and 4). Reaction with *p*–toluenesulfonyl isocyanate proceeded slowly under the reaction conditions and the corresponding amide was obtained in 48% yield (run 5).

Tantalum–alkyne complexes derived from unsymmetrical alkynes produce two regioisomeric amides. Regioselectivities of the reactions between tantalum–alkyne complexes and isocyanates have the same tendency as those between the complexes and aldehydes.[4c] Insertion of isocyanates took place at the less hindered side of the tantalum–alkyne complexes (runs 6–11). In the case of 1–methylthio–1–alkyne the regioisomer **A** was produced exclusively because of the electronic nature of the substituents (runs 12 and 13).[4e]

Reaction of the tantalum–6–dodecyne complex **2** with phenyl isocyanate, followed by iodinolysis with 5 equiv of iodine at −25 °C produced (*Z*)–3–iodo–2–pentyl–2–octenamide **5** in 66% yield stereoselectively (Eq. 2). The structure of amide **5** was ascertained by deiodination of **5** with triethylammonium formate and $Pd(PPh_3)_4$ in DMF at 60 °C.[7]

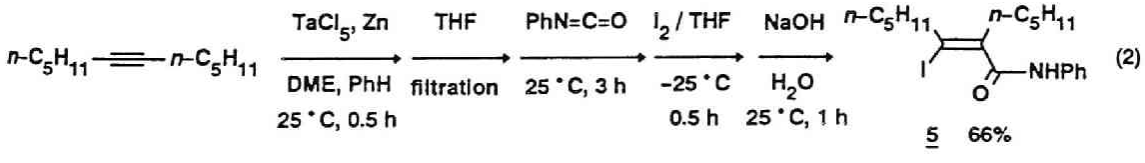
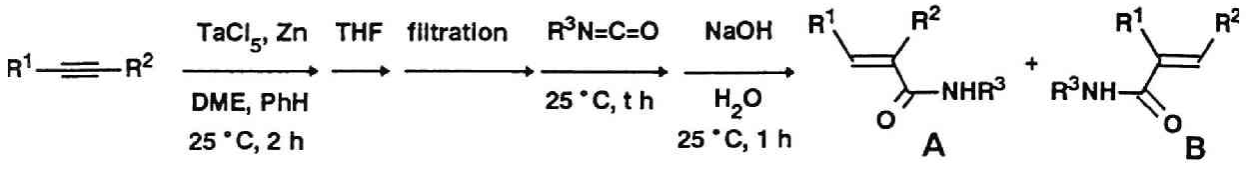


Table 1. Reactions between Alkynes and Isocyanates by Means of $TaCl_5$ and Zinc[a]

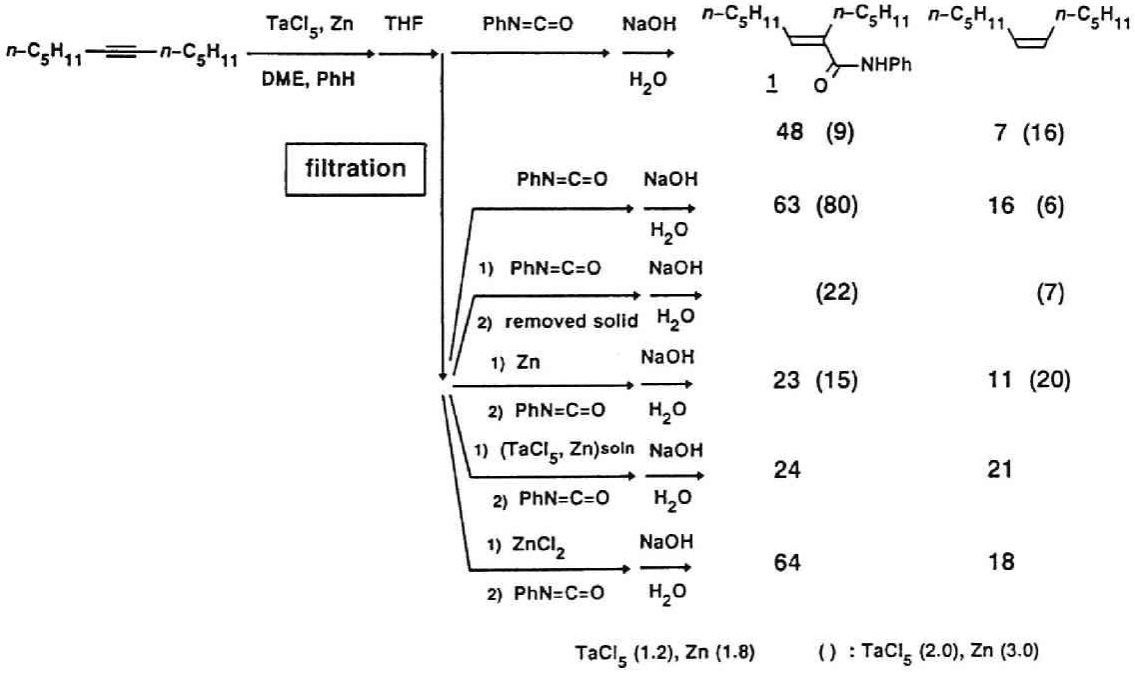


Run	R^1	R^2	R^3	R^3NCO equiv.	Time h	Yield[b] %	A / B[c]
1	n-C_5H_{11}	n-C_5H_{11}	Ph	1.2	3	80 [1]	–
2			Bu	1.2	3	72	–
3			t-Bu	1.2	20	6 (79)	–
4			Me_3Si	1.2	20	<1 (63)	–
5			Ts	1.2	20	48 (29)	–
6	c-C_6H_{11}	n-C_6H_{13}	Ph	2.0	3	69	55 / 45
7			Bu	2.0	3	62	73 / 27
8	Ph	n-C_6H_{13}	Ph	4.0	3	51	60 / 40
9			Bu	4.0	3	74	72 / 28
10	Me_3Si	n-$C_{10}H_{21}$	Ph	4.0	3	60	84 / 16
11			Bu	1.2	3	33	82 / 18
12	MeS	n-$C_{10}H_{21}$	Ph	2.0	0.2	58	>99 / <1
13			Bu	2.0	0.2	90	>99 / <1

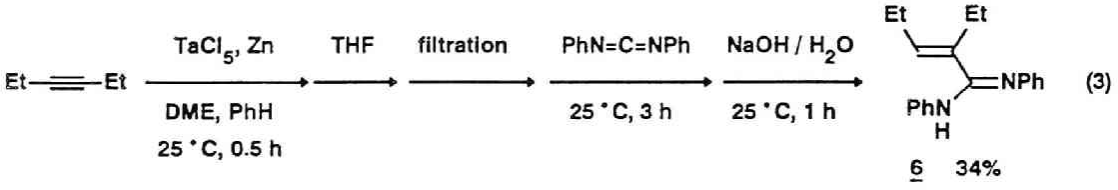
a) Reactions were conducted on 1.0 mmol scale. Two mole of $TaCl_5$ and 3 mol of zinc were employed per mole of an alkyne. b) Isolated yields. Yields of unreacted 6-dodecene are shown in parenthesis. c) Regioisomeric ratios (**A/B**) were determined by ^1H NMR analysis.

To clarify the effect of filtration, the following experiments were conducted (Scheme 1). (1) When the removed solid by filtration was put back to the reacted mixture of tantalum–alkyne complexes and isocyanates, many byproducts appeared and the yield of the desired adduct **1** fell to 22%. (2) Addition of the following compounds into the filtered tantalum–6–dodecyne solution, derived by treatment of 6–dodecyne with 1.2 equiv of tantalum and 1.8 equiv of zinc, before reaction with phenyl isocyanate gave **1** in the following yields in parenthesis. To eliminate the effect of the excess amount of low–valent tantalum, the amount of $TaCl_5$ and zinc was reduced to 1.2 and 1.8 equiv,[8] respectively: Zinc, 1.8 equiv (23%); low–valent tantalum solution, 3 equiv (24%); zinc chloride, 1.8 equiv (64%); none (63%). α,β–Unsaturated amide **1** was obtained in 48% yield under the same conditions without filtration. These results suggest that excess amount of zinc or low–valent tantalum promotes further reactions which consume the initial adduct **3** (or **4**).

Scheme 1



Reaction of the tantalum–6–dodecyne complex with phenyl thioisocynate resulted in recovery of (*Z*)–6–dodecene in 81% yield.[6a] In contrast, tantalum–3–hexyne complex reacted with diphenylcarbodiimide to give (*E*)–α,β–unsaturated amidine **6** in 34% yield (Eq. 3).[6c]



6 34% (3)

Experimental Section

General Procedure for the Synthesis of α,β-Unsaturated Amide. To a pale yellow solution of $TaCl_5$ (0.72 g, 2.0 mmol) in benzene (5 mL) and DME (5 mL) was added zinc dust (0.20 g, 3.0 mmol) at 25 °C under an argon atmosphere. The color of the solution turned greenish dark blue with slightly exothermic process. The resulting mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of alkyne (1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C for 30 min. THF (5 mL) was added to the mixture. After being stirred at 25 °C for 15 min, the mixture was filtered under an argon atmosphere, and the removed solid was washed with THF (2x3 mL). To the combined filtrates was added isocyanate (1.2 mmol), and the resulting mixture was stirred at 25 °C for 3 h. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed well with ethyl acetate (3x5 mL). Organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel gave α,β-unsaturated amide.

***(E)*-*N*-Phenyl-2-pentyl-2-octenamide (1).** R_f=0.62 (ethyl acetate-hexane, 1:5); mp 54-56 °C; bp 130-132 °C (bath temp, 0.20 Torr); IR (neat) 3296, 2924, 2854, 1653, 1598, 1539, 1439, 1324, 752, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.3 Hz, 3H), 0.90 (t, *J*=6.3 Hz, 3H), 1.2-1.6 (m, 12H), 2.16 (dt, *J*=7.3, 7.3 Hz, 2H), 2.37 (t, *J*=7.3 Hz, 2H), 6.26 (t, *J*=7.3 Hz, 1H), 7.07 (dd, *J*=7.6, 7.6 Hz, 1H), 7.29 (dd, *J*=7.6, 7.6 Hz, 2H), 7.57 (d, *J*=7.6 Hz, 2H), 7.7-7.8 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 27.1, 28.1, 28.7, 31.5, 31.7, 119.9, 123.8, 128.7, 135.4, 137.7, 138.3, 168.0. Anal. Calcd for $C_{19}H_{29}NO$: C, 79.39; H, 10.17; N, 4.87. Found: C, 79.62; H, 10.44; N, 4.84.

***(E)*-*N*-Butyl-2-pentyl-2-octenamide.** R_f=0.40 (ethyl acetate-hexane, 1:5);

bp 139–141 °C (bath temp, 0.20 Torr); IR (neat) 3304, 2954, 2924, 2856, 1656, 1620, 1535, 1466, 1307 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.1 (m, 9H), 1.2–1.7 (m, 16H), 2.11 (dt, *J*=7.0, 7.3 Hz, 2H), 2.28 (t, *J*=7.3 Hz, 2H), 3.30 (dt, *J*=5.9, 6.9 2H), 5.6–5.8 (m, 1H), 6.12 (t, *J*=7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.7, 13.9, 20.1, 22.4, 27.1, 27.9, 28.7, 28.8, 31.5, 31.7, 39.3, 134.2, 137.2, 169.7. Anal. Calcd for $C_{17}H_{33}NO$: C, 76.34; H, 12.44; N, 5.24. Found: C, 76.36; H, 12.64; N, 5.24.

***(E)*-*N*-*tert*-Butyl-2-pentyl-2-octenamide.** R_f=0.41 (ethyl acetate–hexane, 1:10); bp 125–127 °C (bath temp, 0.16 Torr); IR (neat) 3314, 2924, 2856, 1657, 1624, 1529, 1453, 1363, 1223 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 6H), 1.2–1.6 (m, 12H), 1.31 (s, 9H), 2.0–2.2 (m, 2H), 2.2–2.4 (m, 2H), 5.4–5.7 (m, 1H), 6.03 (t, *J*=7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 27.2, 28.0, 28.7, 28.8, 29.6, 31.6, 31.8, 51.0, 133.6, 138.2, 169.6. Anal. Calcd for $C_{17}H_{33}NO$: C, 76.34; H, 12.44; N, 5.24. Found: C, 12.43; H, 76.08; N, 5.21.

***(E)*-*N*-*p*-Toluenesulfonyl-2-pentyl-2-octenamide.** R_f=0.65 (ethyl acetate–hexane, 1:2); bp 188–190 °C (bath temp, 0.11 Torr); IR (neat) 3266, 2926, 2856, 1693, 1425, 1189, 812, 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (t, *J*=6.5 Hz, 3H), 0.84 (t, *J*=6.5 Hz, 3H), 1.1–1.5 (m, 12H), 2.0–2.3 (m, 4H), 2.44 (s, 3H), 6.36 (t, *J*=7.3 Hz, 1H), 7.35 (d, *J*=8.5 Hz, 2H), 7.99 (d, *J*=8.5 Hz, 2H), 8.78 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 13.7, 13.8, 21.5, 22.3, 26.3, 28.1, 28.4, 28.5, 31.3, 31.4, 128.2, 129.3, 134.5, 135.7, 141.1, 144.6, 166.3. Anal. Calcd for $C_{20}H_{31}NO_3S$: C, 65.72; H, 8.55; N, 3.83. Found: C, 65.65; H, 8.75; N, 3.81.

***(E)*-*N*-Phenyl-3-cyclohexyl-2-hexylpropenamide.** R_f=0.60 (ethyl acetate–hexane, 1;5); mp 138–140 °C; bp 198–200 °C (bath temp, 0.20 Torr); IR (nujol) 3270, 1731, 1649, 1625, 1324, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.4 Hz, 3H), 1.0–1.5 (m, 12H), 1.6–1.9 (m, 6H), 2.3–2.5 (m, 3H), 6.05 (d, *J*=9.6 Hz, 1H), 7.10 (t, *J*=7.6 Hz, 1H), 7.33 (t, *J*=7.6 Hz, 2H), 7.44 (bs, 1H), 7.56 (d, *J*=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 25.67, 25.73, 25.8, 27.5, 29.3, 29.5, 31.6,

32.7, 37.5, 119.8, 124.0, 128.9, 136.2, 138.2, 140.4, 168.1. Anal. Calcd for $C_{21}H_{31}NO$: C, 80.46; H, 9.97; N, 4.47. Found: C, 80.56; H, 10.08; N, 4.43.

(*E*)-*N*-Phenyl-2-cyclohexyl-2-nonenamide. R_f=0.64 (ethyl acetate-hexane, 1:5); mp 108-110 °C; bp 198-200 °C (bath temp, 0.20 Torr); IR (nujol) 3216, 1731, 1648, 1628, 759, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J*=6.7 Hz, 3H), 1.1-1.6 (m, 12H), 1.6-1.9 (m, 6H), 2.1-2.3 (m, 2H), 2.4-2.6 (m, 1H), 5.88 (t, *J*=7.0 Hz, 1H), 7.10 (t, *J*=7.4 Hz, 1H), 7.27 (s, 1H), 7.33 (t, *J*=7.4 Hz, 2H), 7.54 (d, *J*=7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 25.8, 26.8, 27.5, 29.1, 29.3, 31.0, 31.1, 31.7, 39.0, 119.7, 124.1, 129.0, 132.4, 138.1, 143.9, 175.0. Anal. Calcd for $C_{21}H_{31}NO$: C, 80.46; H, 9.97; N, 4.47. Found: C, 80.39; H, 10.17; N, 4.39.

(*E*)-*N*-Butyl-3-cyclohexyl-2-cyclohexyl-2-propenamide. R_f=0.33 (ethyl acetate-hexane, 1:5); bp 152-154 °C (bath temp, 0.30 Torr); IR (nujol) 3298, 1655, 1618, 1541, 1535, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9-1.0 (m, 6H), 1.1-1.5 (m, 12H), 1.4-1.9 (m, 10H), 2.2-2.4 (m, 3H), 3.30 (dt, *J*=6.3, 6.7 Hz, 2H), 5.7-5.8 (m, 1H), 5.90 (d, *J*=9.8 Hz,1H); ^{13}C NMR ($CDCl_3$) δ 13.8, 14.1, 20.1, 22.6, 25.7, 25.9, 27.4, 29.2, 29.4, 31.7, 31.8, 37.2, 39.4, 139.3. Anal. Calcd for $C_{19}H_{35}NO$: C, 77.76; H, 12.12; N, 4,77. Found: C, 78.03; H, 12.21; N, 4.95.

(*E*)-*N*-Butyl-2-cyclohexyl-2-nonenamide. R_f=0.41 (ethyl acetate-hexane, 1:5); bp 152-154 °C (bath temp, 0.30 Torr); IR (nujol) 3290, 1649, 1618, 1523, 1237 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8-1.0 (m, 6H), 1.1-1.5 (m, 12H), 1.4-1.9 (m, 10H), 2.10 (dt, *J*=7.2, 7.1 Hz, 2H), 2.3-2.5 (m, 1H), 3.25 (dt, *J*=6.3, 6.7 Hz, 2H), 5.4-5.6 (m, 1H), 5.65 (t, *J*=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.8, 14.1, 20.1, 22.6, 25.8, 26.8, 27.3, 29.1, 29.4, 31.2, 31.7, 31.8, 38.8, 39.0, 130.9, 143.8, 169.7. Anal. Calcd for $C_{19}H_{35}NO$: C, 77.76; H, 12.02; N, 4.77. Found: C, 77.53; H, 11.72; N, 4.82.

(*E*)-*N*-Phenyl-2-hexyl-3-phenyl-2-propenamide. R_f=0.30 (ethyl acetate-hexane, 1:5); bp 194-196 °C (bath temp, 0.50 Torr); IR (nujol) 3246, 1643,

1599, 1543, 1499, 751, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, *J*=6.0 Hz, 3H), 1.2–1.5 (m, 6H), 1.5–1.7 (m, 2H), 2.5–2.6 (m, 2H), 7.1–7.3 (m, 2H), 7.3–7.5 (m, 7H), 7.62 (d, *J*=7.6 Hz, 2H), 7.76 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 28.1, 28.9, 29.4, 31.5, 120.0, 124.3, 127.9, 128.4, 128.9, 129.0, 132.6, 135.8, 138.1, 139.8, 168.2. Anal. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.98; H, 8.23; N, 4.52.

(*E*)-*N*-Phenyl-2-phenyl-2-nonenamide. R_f=0.37 (ethyl acetate–hexane, 1:5); bp 194–196 °C (bath temp, 0.50 Torr); IR (neat) 3246, 3300, 2924, 2852, 1671, 1597, 1523, 1439, 1378, 752, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (t, *J*=7.0 Hz, 3H), 1.1–1.4 (m, 6H), 1.3–1.6 (m, 2H), 2.01 (dt, *J*=7.7, 7.3 Hz, 2H), 7.0–7.2 (m, 2H), 7.2–7.4 (m, 5H), 7.4–7.6 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 28.8, 28.9, 29.4, 31.6, 119.8, 124.2, 128.4, 128.8, 129.1, 129.9, 135.4, 137.9, 143.0, 165.6. Anal. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.96; H, 8.30; N, 4.53.

(*E*)-*N*-Butyl-2-hexyl-3-phenyl-2-propenamide (A) and (*E*)-N-butyl-2-phenyl-2-nonenamide (B). The regioisomer ratio (**A**/**B**) was determined by ^1H NMR analysis (**A**/**B**=72/28). R_f=0.27 (ethyl acetate–hexane, 1:5); bp 175–177 °C (bath temp, 0.20 Torr); IR (neat, mixture of **A**/**B**=72/28) 3302, 2926, 2856, 1728, 1648, 1619, 1535, 1465, 1459, 1277, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, *J*=6.6 Hz, 3H), 0.95 (t, *J*=7.3 Hz, 3H), 1.1–1.7 (m, 12H), 1.9–2.0 (m, 2H, **B**), 2.50 (dd, *J*=7.4, 8.2 Hz, 2H, **A**), 3.2–3.3 (m, 2H, **B**), 3.3–3.4 (m, 2H, **A**), 5.3–5.4 (m, 1H, **B**), 6.1–6.2 (m, 1H, **A**), 7.0–7.5 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 13.6, 13.8, 14.0, 19.9, 20.1, 22.5, 27.9, 28.6, 28.8, 29.0, 29.2, 31.5, 31.7, 39.5, 127.5 (**A**), 127.9 (**B**), 128.2 (**A**), 128.4 (**B**), 128.5 (**B**), 128.7 (**A**), 129.7 (**B**), 131.6 (**A**), 135.9 (**B**), 136.1 (**A**), 139.2 (**A**), 141.1 (**B**), 166.5 (**B**), 169.9 (**A**). Anal. Calcd for $C_{19}H_{29}NO$: C, 79.39; H, 10.17; N, 4.87. Found: C, 79.35; H, 10.42; N, 4.90.

(*Z*)-*N*-Phenyl-2-decyl-3-(trimethylsilyl)-2-propenamide. R_f=0.32

(ethyl acetate–hexane, 1:3); bp 167–169 °C (bath temp, 0.25 Torr); IR (neat) 3300, 2952, 2922, 1648, 1597, 1534, 1440, 1249, 858, 838, 734, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9H), 0.88 (t, *J*=6.8 Hz, 3H), 1.2–1.6 (m, 16H), 2.47 (dd, *J*=7.0, 8.0 Hz, 2H), 6.20 (s, 1H), 7.10 (t, *J*=7.7 Hz, 1H), 7.32 (t, *J*=7.7 Hz, 2H), 7.55 (bs, 1H), 7.59 (t, *J*=7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –0.1, 14.1, 22.6, 29.3, 29.4, 29.5, 29.8, 31.9, 32.6, 119.8, 124.1, 128.9, 132.2, 138.1, 154.7, 168.1. Anal. Calcd for $C_{22}H_{37}NOSi$: C, 73.48; H, 10.37; N, 3.89. Found: C, 73.19; H, 10.61; N, 3.83.

(*Z*)-*N*-Phenyl-2-(trimethylsilyl)-2-tridecenamide. R_f=0.20 (ethyl acetate–hexane, 1:3); bp 167–169 °C (bath temp, 0.25 Torr); IR (nujol) 3250, 1638, 1596, 1459, 840, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 9H), 0.90 (t, *J*=6.8 Hz, 3H), 1.2–1.6 (m, 16H), 2.23 (dt, *J*=7.6, 7.2 Hz, 2H), 6.59 (t, *J*=7.6 Hz, 1H), 7.09 (t, *J*=7.7 Hz, 1H), 7.13 (bs, 1H), 7.32 (t, *J*=7.7 Hz, 2H), 7.53 (d, *J*=7.7, 2H); ^{13}C NMR ($CDCl_3$) δ 0.2, 14.1, 22.7, 29.3, 29.4, 29.5, 29.6, 31.9, 96.1, 119.7, 124.0, 129.0, 138.3, 148.3. Anal. Calcd for $C_{22}H_{37}NOSi$: C, 73.48; H, 10.37; N, 3.89. Found: C, 73.28; H, 10.67; N, 3.82.

(*Z*)-*N*-Butyl-2-decyl-3-(trimethylsilyl)-2-propenamide. R_f=0.50 (ethyl acetate–hexane, 1:5); bp 184–186 °C (bath temp, 0.30 Torr); IR (neat) 3298, 2922, 2852, 1636, 1595, 1534, 1466, 1249, 1123, 836, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 9H), 0.88 (t, *J*=6.6 Hz, 3H), 0.94 (t, *J*=7.2 Hz, 3H), 1.2–1.5 (m, 18H), 1.4–1.6 (m, 2H), 2.3–2.4 (m, 2H), 3.30 (dt, *J*=6.3, 6.8 Hz, 2H), 3.2–3.3 (m, 2H), 5.9–6.0 (m, 1H), 6.00 (s, 1H); ^{13}C NMR ($CDCl_3$) δ –0.1, 13.7, 14.1, 20.1, 22.6, 29.3, 29.46, 29.53, 29.8, 31.7, 31.9, 32.6, 39.3, 130.9, 154.5, 170.1. Anal. Calcd for $C_{20}H_{41}NOSi$: C, 70.73; H, 12.17; N, 4.12. Found: C, 70.88; H, 12.42; N, 4.10.

(*Z*)-*N*-Butyl-2-(trimethylsilyl)-2-tridecenamide. R_f=0.46 (ethyl acetate–hexane, 1:5); bp 184–186 °C (bath temp, 0.30 Torr); IR (neat) 3296, 2924, 2852, 1669, 1627, 1532, 1466, 1436, 1285, 1248, 841, 635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s., 9H), 0.88 (t, *J*=6.8 Hz, 3H), 0.93 (t, *J*=7.0 Hz, 3H), 1.2–1.5 (m, 18H), 1.3–

1.6 (m, 2H), 2.1–2.2 (m, 2H), 3.25 (dt, *J*=6.2, 6.8 Hz, 2H), 5.3–5.4 (m, 1H), 6.38 (t, *J*=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.2, 13.8, 14.1, 20.1, 22.7, 28.2, 29.3, 29.4, 29.5, 31.8, 31.9, 39.2, 39.8, 141.2, 147.0, 173.7. Anal. Calcd for $C_{20}H_{41}NOSi$: C, 70.73; H, 12.17; N, 4.12. Found: C, 70.60; H, 12.39; N, 4.17.

(*E*)-*N*-Phenyl-2-decyl-3-methylthio-2-propenamide. R_f=0.32 (ethyl acetate–hexane, 1:5); mp 54–56 °C; bp 214–216 °C (bath temp, 0.60 Torr); IR (nujol) 3288, 1639, 1600, 1534, 1500, 1377, 1317, 754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.2–1.5 (m, 14H), 1.3–1.6 (m, 2H), 2.41 (s, 3H), 2.4–2.5 (m, 2H), 7.22 (s, 1H), 7.10 (t, *J*=7.8 Hz, 1H), 7.33 (t, *J*=7.8 Hz, 2H), 7.42 (bs, 1H), 7.94 (d, *J*=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 17.3, 22.7, 27.9, 29.2, 29.3, 29.4, 29.6, 31.9, 120.0, 124.2, 129.0, 131.4, 138.0, 139.2, 164.5. Anal. Calcd for $C_{20}H_{31}NOS$: C, 72.02; H, 9.37; N, 4.20. Found: C, 72.02; H, 9.37; N, 4.20.

(*E*)-*N*-Butyl-2-decyl-3-methylthio-2-propenamide. R_f=0.16 (ethyl acetate–hexane, 1:3); bp 186–188 °C (bath temp, 0.50 Torr); IR (neat) 3310, 2922, 2852, 1734, 1624, 1533, 1466, 1377, 1288, 734 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 0.93 (t, *J*=7.1 Hz, 3H), 1.2–1.5 (m, 18H), 1.4–1.6 (m, 2H), 2.30 (t, *J*=7.4 Hz, 2H), 2.38 (s, 3H), 3.31 (dt, *J*=5.9, 5.9 Hz, 2H), 5.7–5.8 (m, 1H), 7.10 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.7, 14.0, 17.1, 20.1, 22.6, 27.9, 28.9, 29.2, 29.4, 29.5, 31.7, 31.8, 39.5, 131.0, 137.5, 166.2. Anal. Calcd for $C_{18}H_{35}NOS$: C, 68.95; H, 11.25; N, 4.47. Found: C, 69.11; H, 11.50; N, 4.54.

(*Z*)-*N*-Phenyl-3-iodo-2-pentyl-2-octenamide (5). To a stirred solution of $TaCl_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and benzene (1:1, 10mL) at 25 °C under an argon atmosphere was added zinc dust (0.20 g, 3.0 mmol), and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 6–dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C for 30 min. THF (5 mL) was added to the mixture. After being stirred at 25 °C for 15 min, the mixture was filtered under an

argon atmosphere, and the removed solid was washed with THF (2x3 mL). To the combined filtrates was added phenyl isocyanate (0.14 g, 1.2 mmol), and the resulting mixture was stirred at 25 °C for 3 h. To the mixture was added at −25 °C a solution of iodine (1.3 g, 5.0 mmol) in THF (6 mL), and the whole mixture was stirred at −25 °C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added at 25 °C, and the mixture was stirred at 25 °C for additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3x5 mL). The organic extracts were washed with saturated $NaHSO_3$ (10 mL) and brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by column chromatography on silica gel with ethyl acetate–hexane (1:10) gave 0.27 g (66%) of (*Z*)-*N*-phenyl-3-iodo-2-pentyl-2-octenamide. R_f=0.62 (ethyl acetate–hexane, 1:5); bp 166–168 °C (bath temp, 0.18 Torr); IR (neat) 3274, 3130, 3056, 1653, 1599, 1540, 1441, 1328, 754, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, *J*=6.6 Hz, 3H), 0.91 (t, *J*=6.6 Hz, 3H), 1.2–1.5 (m, 8H), 1.4–1.8 (m, 4H), 2.42 (t, *J*=8.0 Hz, 2H), 2.54 (t, *J*=7.5 Hz, 2H), 7.12 (dd, *J*=7.4, 7.4 Hz, 1H), 7.32 (dd, *J*=7.4, 7.4 Hz, 2H), 7.4–7.6 (bs, 1H), 7.57 (d, *J*=7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 22.3, 22.4, 28.3, 28.9, 30.7, 31.5, 31.9, 40.5, 103.8, 120.1, 124.5, 128.9, 137.4, 144.9, 169.2. Anal. Calcd for $C_{19}H_{28}INO$: C, 55.21; H, 6.83; N, 3.39. Found: C, 55.39; H, 6.82; N, 3.45.

Procedure for Deiodination of 5.[7] To a mixture of the α,β-unsaturated amide **5** (0.41 g, 1.0 mmol), Et_3N (0.42 mL, 3.0 mmol), and $Pd(PPh_3)_4$ (23 mg, 0.020mmol) in DMF (2 mL) was added formic acid (0.075 mL, 2.0 mL). The mixture was stirred at 60°C for 1h under an argon atmosphere. The reaction mixture was poured into brine (15 mL), and extracted with ether (2x10 mL). The organic layer was washed with brine (10 mL) and dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel using ethyl acetate–hexane (1:20) as eluent gave 0.28 g (96 %) of the amide **1**.

(*E*)-N^1,N^2-diphenyl-2-ethyl-2-pentenamidine (6). To a stirred solution of $TaCl_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and benzene (1:1, 10mL) at 25 °C under an argon atmosphere was added zinc dust (0.20 g, 3.0 mmol) and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 3-hexyne (0.082 g, 1.0 mmol) in DME and benzene (1:1, 2 mL) and the whole mixture was stirred at 25 °C for 30 min. THF (5 mL) was added to the mixture. After being stirred at 25 °C for 15 min, the mixture was filtered under an argon atmosphere and the removed solid was washed with THF (2x3 mL). To the combined filtrates was added diphenylcarbodiimide (0.24 g, 1.2 mmol)[9] and the resulting mixture was stirred at 25 °C for 3 h. Aqueous NaOH solution (15%, 2 mL) was added and the mixture was stirred at 25 °C for additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed well with ethyl acetate (3x5 mL). Organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica gel with ethyl acetate-hexane (1:10) gave 94 mg (34%) of amidine **6**: R_f=0.45 (ethyl acetate-hexane, 1:5); mp 77-79 °C; bp 152-154 °C (bath temp, 0.20 Torr); IR (nujol):3254, 1730, 1586, 1534, 1271, 1122, 1071, 754, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, J=7.4 Hz, 3H), 0.97 (t, J=7.5 Hz, 3H), 1.7-1.9 (m, 2H), 2.0-2.2 (m, 2H), 6.1-6.3 (m, 1H), 6.3-6.6 (m, 1H), 7.2-7.5 (m, 4H), 7.4-7.8 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 12.7, 13.6, 20.7, 21.3, 120.2, 120.8, 121.38, 121.43, 121.5, 122.2, 128.6, 135.8, 137.9, 139.0, 155.8. Anal. Calcd for $C_{19}H_{22}N_2$: C, 81.97; H, 7.97; N, 10.06. Found: C, 81.68; H, 7.94; N, 10.00.

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Publication List

I. Parts of the present thesis have been, or are to be, published in the followingjournals.

Chapter 2	*Tetrahedron Lett.* **1990**, *31*, 365.
	J. Org. Chem. in press.
Chapter 3	*J. Org. Chem.* **1990**, *55*, 1707.
	J. Org. Chem. in press.
Chapter 4	*J. Org. Chem.* in press.
Chapter 5	*Tetrahedron Lett.* **1990**, *31*, 369.
Chapter 6	*Organometallics* **1990**, *9*, 3030.
Chapter 7	*J. Org. Chem.* **1990**, *55*, 5310.
	Tetrahedron in press.
Chapter 8	*Chem. Lett.* **1991**, 1479.

II. Other publications not included in this thesis.

(1) Stereoselective Synthesis of (*E*)-Alkenylsilanes from Aldehydes with a Reagent Prepared by Chromium(II) Reduction of $Me_3SiCHBr_2$.
Takai, K.; Kataoka, Y.; Okazoe, T.; Utimoto, K.
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(2) Regio- and Stereoselective Preparation of Silyl Enol Ethers by Alkylidenation of Silyl Esters.
Takai, K.; Kataoka, Y.;Okazoe, T.; Utimoto, K.
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(3) Preparation of Alkenyl Sulfides and Enamines by Alkylidenation of Carboxylic Acid Derivatives.
Takai, K.; Fujimura, O.; Kataoka, Y.; Utimoto, K.
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(4) Stereoselective Addition of α-Chloro Allylic Chromium Reagents to Aldehydes.
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(5) Preparation of β-Hetero-Substituted Alkenylsilanes from Carboxylic Acid Derivatives.
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